CANADIAN JOURNAL OF RESEARCH

VOLUME 26
1948
SECTION F

CANADA

Published by the
NATIONAL RESEARCH COUNCIL *of* CANADA

Canadian Journal of Research

Issued by The National Research Council of Canada

VOL. 26, SEC. F. JANUARY, 1948 NUMBER 1

CANADIAN WILTSHIRE BACON

XXVIII. CHLORIDE SHIFT IN CURED PORK[1]

By G. A. Grant[2] and N. E. Gibbons[3]

Abstract

Carefully conducted flavor tests and chemical analyses for chloride ion showed that bacon of the Wiltshire type increased in saltiness and water extractable chloride during storage. Enzyme digests of freshly cured pork gave higher chloride recoveries than those obtained in water extraction procedures. On the other hand, recovery of sodium ion in freshly cured material was identical by water extraction, enzyme digestion, or a wet ashing procedure. These results show that the chloride ion is bound by the muscle constituents and that it can be released by enzyme action. This mechanism would explain the increase in saltiness observed in stored bacon.

Introduction

The most serious complaint against Canadian bacon exported to England is its excessive saltiness. This has been supported by flavor tests conducted in England (7). Although it is generally recognized that curing practice is largely responsible for the saltiness of the product, commercial operators have claimed that bacon of the Wiltshire type increases in saltiness during storage. If this is true, then the saltiness of Canadian bacon increases before it is consumed in England. Hence it was thought advisable to investigate the effect of aging on saltiness and to study some of the changes taking place in the muscle tissue.

Experimental and Results

The material in the first experiment consisted of rib-in export backs from 20 hogs. The backs were cut in half and two half-backs allotted at random to each experimental condition. The half-backs were cured to contain 0.2% nitrate at sodium chloride levels of 2, 3, 4, 5, and 6%, and 0.1% nitrate at sodium chloride levels of 2, 4, and 6%. For the material to contain 0.2% nitrate, the pump pickle contained 30% sodium chloride, 1.5% nitrate, and 0.05% nitrite, while the cover pickle contained 28% sodium chloride, 1.5% nitrate, and 0.05% nitrite. Material to contain 0.1% nitrate was cured in similar curing pickles except that the nitrate concentration was reduced to

[1] *Manuscript received September 10, 1947.*

Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa, Canada. This material was presented at the annual convention of the Chemical Institute of Canada, June 9, 1947. Issued as Paper No. 196 of the Canadian Committee on Food Preservation and as N.R.C. No. 1657.

[2] *Technical Officer, Food Investigations.*

[3] *Bacteriologist, Food Investigations.*

0.5%. Different sodium chloride levels were obtained by varying the amount of pickle pumped into each half-back and by the time in cure. The material was cured in small tanks for two to four days at 4.4° C. (40° F.) and at a pickle to meat ratio of 20 gal. per 100 lb.

After removal from cure, the pieces were wrapped in waxed paper, overwrapped in brown kraft, and stored at −1.1° C. (30° F.). Samples were removed from storage at 0, 6, 12, 18, and 24 days and prepared for chemical and biological determinations. Half-backs were sampled as follows: bones were removed and the back cut into slices ¼ in. thick. The slices were then randomized into three lots for chemical analyses, taste panel assessments, and vitamin analyses. Chemical analyses were also done on the cooked samples. The work on the vitamin analyses will be reported in a separate paper (1). The material for chemical and vitamin analyses was trimmed free of most of the fat, minced three times in a food chopper, frozen at −40° C., and stored at that temperature until required for analysis. After the material was thawed, chloride (6), nitrate (4), and moisture contents (6) were determined. Flavor was determined as follows: small pieces of the meat were trimmed free of fat and grilled at 260° C. (500° F.) on a wire screen for six minutes (three minutes on each side). Saltiness was assessed on the following scale: −1 to −5, deficiency; 0, ideal; + 1 to + 5, excess saltiness. The scoring panel of 15 people was required to score no more than four samples in any morning or afternoon.

Chloride and nitrate contents of the lean meat for each experimental cure, averaged over all storage times, are given in Table I. It is evident that a range of salt concentrations from 3.8 to 5.7% and two levels of nitrate, 0.1% and 0.2%, were obtained in curing the material.

TABLE I

MEAN CHLORIDE AND NITRATE CONTENTS OF WILTSHIRE BACON FROM SEVERAL CURES, AFTER STORAGE AT −1.1° C. (30° F.) FOR 24 DAYS

(Values averaged over all storage times)

Desired nitrate level, %	Desired chloride level, %	Chloride,[a] %		Nitrate,[a] %	
		Raw	Cooked	Raw	Cooked
0.2	2	3.86	6.29	0.16	0.27
	3	4.74	7.05	0.20	0.30
	4	5.01	7.60	0.24	0.37
	5	5.27	7.70	0.21	0.34
	6	5.60	8.13	0.25	0.38
0.1	2	4.35	6.52	0.06	0.09
	4	5.07	7.73	0.06	0.10
	6	5.70	8.53	0.07	0.11
Necessary difference[b]		0.58	0.74	0.027	0.027

[a] *Calculated as the sodium salt.*
[b] *Necessary difference to exceed the 5% level of statistical significance.*

As it is difficult to cure any two pieces of meat to contain exactly the same salt content, the difference between duplicate samples may be large. Hence statistical analyses of the data were employed to establish the significance of any trends obtained in storage. Table II shows the results of an analysis of variance: the time of storage had significant effects on the chloride and nitrate contents and on flavor, the moisture content was unaffected, and all the salt levels behaved similarly. The magnitude and direction of the significant effects are given in Table III. Flavor scores showed a significant

TABLE II

ANALYSIS OF VARIANCE FOR THE EFFECTS OF STORAGE ON THE CHLORIDE, NITRATE, AND MOISTURE CONTENTS AND THE FLAVOR OF WILTSHIRE BACON STORED FOR 24 DAYS AT $-1.1°$ C. (30° F.)

Source of variance	Degrees of freedom	Mean square						
		Chloride		Nitrate		Moisture		Flavor
		Raw	Cooked	Raw	Cooked	Raw	Cooked	
Cures	7	3.8**	5.9**	0.066**	0.155**	0.7	16.0	1.50**
Time	4	2.1**	5.2**	0.008**	0.039**	2.6	1.7	2.20**
Cures × time	28	0.4	0.6	0.001	0.003	0.8	10.4	0.14
Between duplicates	40	0.4	0.7	0.002	0.002	1.4	25.9	0.27

** *Indicates 1% level of statistical significance.*

TABLE III

EFFECTS OF TIME OF STORAGE ON THE MEAN CHLORIDE AND NITRATE CONTENTS AND FLAVOR SCORE OF WILTSHIRE BACON STORED AT $-1.1°$ C. (30° F.) FOR 24 DAYS

(Values averaged over all cures)

Time, days	Chloride,[a] %		Nitrate,[a] %		Flavor score[b]
	Raw	Cooked	Raw	Cooked	
0	4.44	6.68	0.13	0.17	0.7
6	4.73	7.04	0.14	0.26	0.9
12	5.09	7.66	0.17	0.23	1.3
18	5.15	7.82	0.16	0.27	1.6
24	5.35	8.03	0.18	0.30	1.6
Necessary difference[c]	0.46	0.56	0.027	0.024	0.4

[a] *Calculated as the sodium salt.*
[b] *Saltiness ratings only.*
[c] *Necessary difference to exceed the 1% level of statistical significance.*

increase in saltiness during storage, first evident after 12 days. This coincided with significant increases in chloride and nitrate contents of both the cooked and uncooked meat. From these results the increase in saltiness on storage appears to be real and substantial.

Comparison of Analytical Methods

It was necessary to consider the analytical methods involved and to check the results of the previous experiment by employing another analytical procedure. The investigations of White (6) on cured meat showed that ashing the meat by the A.O.A.C. method and titrating by the Volhard procedure (3) produced lower chloride values than extracting the meat with hot water and titrating by the Mohr procedure (6). There are two possible explanations for these results; underestimation of chloride by loss of chlorine during ignition of the meat in the ashing procedure or the overestimation of chloride ion by titration of materials other than chloride in the water extract of the meat. The latter was checked by adding known amounts of pure sodium chloride to water extracts of fresh pork. Complete recoveries of the chloride ion were obtained. Therefore it was assumed that, owing to loss of chlorine during ignition, the ashing procedure underestimates chloride content and that water extraction and direct titration is the better procedure.

The increase in chloride content of stored bacon was rechecked by the ashing and water extraction procedures. The results are given in Table IV.

TABLE IV

THE ESTIMATION OF SODIUM CHLORIDE IN WILTSHIRE BACON STORED FOR 0 AND 24 DAYS AT $-1.1°$ C. (30° F.) BY DRY ASHING AND WATER EXTRACTION PROCEDURES

(Means of duplicate determinations)

Sample No.	Sodium chloride, %			
	Dry ashing		Water extraction	
	0 days	24 days	0 days	24 days
1	2.1	3.3	2.4	3.5
2	3.5	4.7	3.6	5.1
3	4.8	5.8	4.9	6.2

The chloride content as determined by the ashing procedure was lower than that determined by water extraction. This is in agreement with the previous results reported by White (6). Although the chloride values obtained by the two methods were different the increase in chloride content on storage of bacon was evident by both procedures. Therefore the increase in saltiness of bacon on storage does not depend on the analytical procedure used to estimate the chloride ion.

Diffusion of Chloride or Moisture from Fat to Lean

As only the lean meat had been analyzed it was possible that chloride and nitrate had diffused from the fat to the lean. This was investigated but since nitrate is unstable owing to bacterial action, only changes in the chloride were followed.

This experiment employed six export backs divided into 30 pieces. The pieces were cured to give sodium chloride contents of 2, 4, and 6%, then stored and sampled as in the previous experiment. Chloride and moisture contents were determined on the fat and lean portions of each piece. Moisture content in the fat and lean and chloride content in the lean were determined as previously described (6). Chloride content in the fat was determined according to the method of the A.O.A.C. (3) in which the sample is ashed, leached with hot water, and the chloride of the extract determined by the Mohr procedure.

Chloride and moisture contents of the fat and lean meat for each cure, averaged over all storage times, are given in Table IV. It is evident that only small amounts of chloride and moisture diffuse into fat during curing. Statistical analysis of the data shows that the time of storage had a significant effect on the chloride content of both lean and fat (Table V). As pork fat

TABLE V

CHLORIDE AND MOISTURE CONTENTS OF THE LEAN AND FAT OF WILTSHIRE BACON STORED AT −1.1° C. (30° F.) FOR 24 DAYS

(Mean values averaged over all other conditions)

Desired chloride levels, %	Lean meat		Fat	
	Chloride, %	Moisture, %	Chloride, %	Moisture, %
2	2.82	71.6	0.37	7.68
4	4.44	71.2	0.59	7.52
6	6.10	70.9	0.63	7.33
Necessary difference[a]	0.56	0.86	0.14	1.02

[a] *Necessary difference to exceed the 1% level of statistical significance.*

contains appreciable amounts of connective tissue, it is not surprising that it exhibits somewhat the same behavior as lean meat. It is evident that the increase in water extractable chloride could not be attributed to diffusion of the chloride or moisture from the fat to the lean.

Release of Bound Chloride by Enzymes

The increase in water extractable chloride on storage may be explained by fixation of a portion of the chloride by the freshly cured muscle and subsequent release of chloride through enzyme action, or otherwise. As it was possible that fixation of either the sodium or chloride ion, or both, may have occurred, both sodium and chloride were determined on freshly cured pork in the next experiment.

Freshly cured backs were trimmed free of fat and bone, minced, and samples subjected to water extraction, enzyme digestion, and wet ashing procedures. Water extraction was carried out by a previously described method (6). In the enzyme digest procedure, 10 gm. of meat was digested for 18 hr. at 37° C. with 0.2 gm. of papain and 0.2 gm. of takadiastase in 100 ml. of solution adjusted to pH 4.6. Wet ashing was done with concentrated sulphuric and nitric acids. Chloride was determined by the Mohr procedure and sodium by precipitation as sodium zinc uranyl acetate (5, p. 878). From Table VI, it is

TABLE VI

EFFECTS OF STORAGE ON THE CHLORIDE AND MOISTURE CONTENTS OF THE FAT AND LEAN PORTIONS OF WILTSHIRE BACON STORED AT −1.1° C. (30° F.) FOR 24 DAYS

(Mean values averaged over all other conditions)

Time, days	Lean meat		Fat	
	Chloride,[a] %	Moisture, %	Chloride,[a] %	Moisture, %
0	3.64	72.3	0.37	7.31
6	4.21	71.5	0.41	7.64
12	4.85	70.6	0.48	7.08
18	4.62	71.0	0.67	8.43
24	4.94	70.7	0.68	7.05
Necessary difference[b]	0.72	1.11	0.14	0.39

[a] *Calculated as the sodium salt.*
[b] *Necessary difference to exceed the 1% level of statistical significance.*

evident that the recovery of the sodium was similar by water extraction, enzyme digestion, or wet ashing procedures, but that digestion with papain and takadiastase gave higher recoveries of chloride than the water extraction procedure. These results show that the chloride is bound by the muscle tissues, that it can be released by enzyme action, and that the sodium ion is not bound.

TABLE VII

CHLORIDE AND SODIUM CONTENTS OF FRESHLY CURED WILTSHIRE BACON BY DIFFERENT METHODS OF ANALYSIS

Sample No.	Sodium, %			Chloride, %		Chloride, %
	Water extract	Enzyme digest	Wet ash	Water extract	Enzyme digest	Difference between enzyme digest and water extract
1	0.73	0.80	0.81	1.22	1.52	0.30
2	0.94	0.95	0.93	1.48	1.96	0.48
3	2.05	2.06	2.06	3.19	3.63	0.44

Discussion

The increase in saltiness in cured pork may be satisfactorily explained as follows: while pork is curing in brine solution, some of the chloride ions are bound by the muscle tissues while the sodium ions remain in the outer tissue fluid with the excess sodium chloride. When the cured pork is stored, bacterial or autolytic enzymes or both break down the muscle tissue and the chloride is released. The freed chloride then reunites with the sodium to form sodium chloride. If it is assumed that the bound chloride is not released on mastication, this mechanism satisfactorily explains the increase in saltiness that occurs in stored bacon. An increase in nitrate also occurred during storage, and it is possible that the nitrate ion is behaving similarly to the chloride ion. This would further enhance the saltiness during storage, as it has been shown that sodium nitrate imparts a salty flavor to cured products (2). As the concentrations of potassium and other ions were not determined, no calculations have been made to determine the amount of chloride bound by the muscle tissue or accounted for as sodium chloride. More work is required to ascertain the concentration of chloride that is bound by the muscle tissue, and the factors governing the reaction.

Acknowledgments

The authors wish to express their thanks to Dr. J. W. Hopkins, Statistician, for statistical assistance, and to Messrs. W. H. McNaughton and J. M. McLaughlan, Laboratory Assistants, for technical aid.

References

1. GORHAM, P. Can. J. Research, F, 26 : 8-13. 1948.
2. HOPKINS, J. W. Can. J. Research, F, 25 : 29-33. 1947.
3. KERR, R. H. J. Assoc. Official Agr. Chem. 16 : 543-546. 1933.
4. MACDOUGALL, D. In preparation.
5. SCOTT, W. W. Standard methods of chemical analysis. Vol. 1. 5th ed. *Ed. by* N. H. Furman. D. Van Nostrand Company, Inc., 1939.
6. WHITE, W. H. Can. J. Research, D, 17 : 125-136. 1939.
7. WINKLER, C. A. and COOK, W. H. Can. J. Research, D, 19 : 157-176. 1941.

CANADIAN WILTSHIRE BACON

XXIX. CHANGES IN THE THIAMINE, RIBOFLAVIN, AND NIACIN CONTENTS PRODUCED BY CURING, STORAGE, AND COOKING[1]

By Paul R. Gorham[2]

Abstract

Significant amounts of thiamine and niacin, but not of riboflavin, were lost during the process of curing pork half-backs in brine pickle on a semicommercial scale. This loss was not related to the final chloride or nitrate content of the meat. Cured half-backs stored at 30° F. (−1.1° C.) for 24 days lost significant amounts of thiamine and riboflavin, but the niacin content remained unchanged. Curing caused a significant increase in the percentage of niacin retained after cooking. During the storage of cured half-backs, the percentage of thiamine retained after cooking increased significantly.

Introduction

As part of an extensive series of investigations of Canadian Wiltshire bacon aimed at improving the quality of the product being shipped overseas, a study was undertaken of the losses of three of the more important B-vitamins arising from the use of different curing pickles, storage, and cooking.

Jackson *et al.* (5) found that with the "wet cure" method of processing bacon the loss of thiamine and niacin exceeded that of riboflavin, while in "dry cured" bacon the greatest loss occurred with riboflavin. Little or no information was available on changes in the B-vitamin content of bacon caused by storage or cooking.

Materials and Methods

In the preceding paper (2) full details have been given of the curing, storage, cooking, and sampling of the 80 half-backs of pork from which samples were obtained for vitamin analyses. These half-backs were cured to produce final chloride contents ranging from 2 to 6% at nitrate levels of 0.1% and 0.2%. Duplicate half-backs from each of the eight cures were withdrawn from storage at 30° F. every six days. Fat and fiber were trimmed away and the lean meat uniformly sliced. The slices from each half-back were distributed at random into four equal lots, of which two were available for vitamin analyses. Of these, one lot was thoroughly ground and mixed by two passages through a meat grinder, while the slices in another lot were cooked by broiling in a domestic electric oven for three minutes on each side and then ground. The ground samples were stored at −40° F. pending analysis.

[1] *Manuscript received September 2, 1947.*

Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa, Canada. Issued as Paper No. 197 of the Canadian Committee on Food Preservation and as N.R.C. No. 1658.

[2] *Biochemist, Food Investigations.*

Four uncured half-backs were treated in a comparable manner to provide samples of fresh and cooked pork for analysis.

Samples were withdrawn from −40° F. and allowed to thaw for 24 hr. at 40° F. A 15 gm. portion of uncooked or a 10 gm. portion of cooked material was extracted with papain and takadiastase and made up to a volume of 200 ml. (7). A dilution of 25 ml. per 100 ml. was used for the assay of thiamine by a modification (11) of the thiochrome method (4, 10). Riboflavin was assayed fluorometrically, using the antimony trichloride–ethanol procedure (7). A dilution of 2.5 ml. per 100 ml. was used for the microbiological assay of niacin by the method of Krehl, Strong, and Elvehjem (6).

Moisture determinations, made on the ground samples by vacuum-drying at 100° C. (2), were used to calculate the results on a moisture-free basis. Changes caused by cooking were expressed as the percentage vitamin retained.

Results

Fresh pork was found to contain, on the average, 66 μgm. of thiamine, 6μgm. of riboflavin, and 220 μgm. of niacin per gram dry weight. As was expected from work reported by others (1, 13), different carcasses contained different amounts of the three vitamins; the percentage retained after cooking also showed a considerable degree of variability (Table I).

TABLE I

VITAMIN CONTENT OF FRESH PORK AND PERCENTAGE RETAINED AFTER COOKING

(Values represent means of duplicate determinations)

Half-back	Uncooked			Cooked		
	μgm./gm. dry wt.			Percentage retained		
	Thiamine	Riboflavin	Niacin	Thiamine	Riboflavin	Niacin
1	68.3	5.55	213.3	59.0	76.6	69.9
2	79.0	6.84	258.6	65.0	77.2	71.4
3	52.8	6.48	229.5	75.8	75.5	66.3
4	64.4	5.04	177.7	77.7	86.7	68.8
Mean	66.1	5.98	219.8	69.4	79.0	69.1

Analyses of variance were used to determine whether significant losses of vitamins occurred during the curing process, and whether the percentage retained after cooking was affected. The results are presented in Table II. Curing caused significant losses of thiamine and niacin but caused little change

in riboflavin content. The percentage of all three vitamins retained after cooking was somewhat higher in cured pork than in uncured pork, but the difference was significant for niacin only.

TABLE II

THE EFFECT OF THE CURING PROCESS UPON THE VITAMIN CONTENT OF PORK AND THE PERCENTAGE RETAINED AFTER COOKING

Treatment	Uncooked			Cooked		
	μgm./gm. dry wt.			Percentage retained		
	Thiamine	Riboflavin	Niacin	Thiamine	Riboflavin	Niacin
Uncured[a]	66.1	5.98	219.8	69.4	79.0	69.1
Cured[b]	51.9	5.82	152.0	77.0	86.2	80.9
Necessary difference, 5% level	12.6	—	54.3	—	—	9.3

[a] *Values represent means of four determinations in duplicate.*
[b] *Values represent means of 16 determinations.*

The vitamin contents of samples subjected to various cures did not differ significantly. However, there were significant differences in the percentage of riboflavin and niacin retained after cooking, the highest retentions being associated with low chloride content (Table III).

TABLE III

THE EFFECT OF DIFFERENT CURES UPON THE PERCENTAGE OF THREE VITAMINS RETAINED AFTER COOKING

(Each value represents the mean of 10 determinations)

Vitamin	Nitrate, 0.2%					Nitrate, 0.1%			Necessary difference, 5% level
	Chloride, %					Chloride, %			
	2	3	4	5	6	2	4	6	
Thiamine	83.7	83.3	78.8	72.1	84.7	82.8	85.1	77.8	—
Riboflavin	94.0	90.2	87.7	80.5	86.9	86.8	92.5	85.5	6.5
Niacin	87.6	89.6	84.7	79.6	81.3	91.0	85.2	84.0	7.5

There was a significant loss of thiamine and riboflavin, but not of niacin, from cured pork stored at 30° F. for 24 days (Table IV). During this period the percentage of thiamine retained after cooking gradually increased until the difference attained statistical significance. No such increase occurred with riboflavin or niacin.

TABLE IV

THE EFFECT OF STORAGE AT 30° F. UPON THE VITAMIN CONTENT OF CURED PORK AND THE PERCENTAGE RETAINED AFTER COOKING

(Each value represents the mean of 16 determinations)

Vitamin	Storage time, days					Necessary difference, 5% level
	0	6	12	18	24	
	μgm./gm. dry wt.					
Thiamine	51.9	38.9	46.0	41.4	37.8	9.5
Riboflavin	5.82	5.31	5.39	5.64	4.78	0.58
Niacin	152.0	162.4	151.5	164.9	150.4	—
	Percentage retained after cooking					
Thiamine	77.0	78.3	75.3	88.6	85.8	7.5
Riboflavin	86.2	87.8	87.6	87.7	90.8	—
Niacin	80.9	86.2	83.1	88.8	87.7	—

Discussion and Conclusions

The loss of significant amounts of thiamine and niacin during the curing process (Table II) suggests that these two vitamins leach into the pickle, whereas riboflavin does not. After pork hams have been wet-cured and smoked, they have been found to lose more thiamine than niacin or riboflavin (16, 17). It was thought possible that differences in vitamin content between the present materials, subjected to eight different cures, might have been obscured, in part, by occasional failure to attain the desired chloride levels. However, even when the actual chloride contents are considered there is still no well-defined relation between vitamin content and the chloride or nitrate content of the cured pork.

The average vitamin retentions during the storage of pork products, reported by various investigators, are shown in Table V. Rice, Fried, and Hess (14) found that ground flank muscle spoiled after storage for 14 days at 40° F. They attributed subsequent high vitamin retentions to synthesis by spoilage microorganisms. Under approximately comparable conditions of storage, cured half-backs lost somewhat more thiamine than fresh hams, fresh loins, or fresh or cured ground flank muscle; all lost about the same amount of riboflavin; but, unlike fresh hams, fresh loins, or cured ground flank muscle, cured half-backs lost no niacin.

Losses of thiamine, niacin, and riboflavin occur during the cooking of fresh pork (1, 8, 9, 12, 14, 15, 16). These losses increase the more the pork is cooked, with loss of thiamine greatly exceeding losses of the other two vitamins (5). Under the cooking conditions used in these experiments, both in uncured and cured pork, the percentages of thiamine and niacin retained were about

TABLE V

RETENTIONS OF THIAMINE, RIBOFLAVIN, AND NIACIN IN STORED PORK PRODUCTS REPORTED BY VARIOUS INVESTIGATORS

Source of data	Material	Storage conditions		Average retention, %		
		Temp., °F.	Time, days	Thiamine	Riboflavin	Niacin
Schweigert, McIntire, and Elvehjem (16)	Fresh hams	24.8	14	92	85	92
Rice, Fried, and Hess (14)	Fresh loins	40	6	101	93	81
			10	107	100	63
			20	95	90	64
			68	97	94	78
	Ground flank muscle	40	7	95	100	102
			14	93	104	97
			21	95	118	97
			28	87	154	101
	Ground flank muscle, nitrate–nitrite–glucose cured	40	14	95	105	90
			56	91	120	93
Gorham (calculated from Table IV)	Half-backs, sodium chloride–nitrate–nitrite cured	30	6	75	91	106
			12	89	93	100
			18	80	97	108
			24	73	82	99

equal and lower than the percentage of riboflavin retained (Table II). The higher percentage of niacin retained after cooking in cured than in uncured samples may bear some relation to the type of cure since it decreased as the sodium chloride content increased (Table III). Initially, the percentage of thiamine retained after cooking was not significantly affected by curing (Table II), as Greenwood and associates have reported (3), but, during subsequent storage, the thiamine retained after cooking increased to a significant degree (Table IV). There is need for further study of curing as it affects the amount of vitamin retained after cooking. The variability observed in the present study may be reduced by the use of a more rigidly standardized cooking procedure.

These experiments, conducted on a semicommercial scale, indicate that an appreciable loss of thiamine, riboflavin, and niacin occurs during the curing of pork in fresh brine pickle and its subsequent storage at 30° F. In commercial practice, however, where many whole backs are cured in brine that is used repeatedly, the losses may not be as great.

Acknowledgments

The author wishes to thank Mr. G. A. Grant and Dr. N. E. Gibbons, who made available most of the ground samples for analysis, and Dr. J. W. Hopkins for statistical services. The technical assistance of Jessie R. Lewis and R. E. de Champlain is also acknowledged.

References

1. Brady, D. E., Peterson, W. J., and Shaw, A. O. Food Research, 9 : 400-405. 1944.
2. Grant, G. A. and Gibbons, N. E. Can. J. Research, F, 26 : 1-7. 1948.
3. Greenwood, D. A., Beadle, B. W., and Kraybill, H. R. J. Biol. Chem. 149 : 349-354. 1943.
4. Harris, L. J. and Wang, Y. L. Biochem. J. 35 : 1050-1067. 1941.
5. Jackson, S. H., Crook, A., Malone, V., and Drake, T. G. H. J. Nutrition, 29 : 391-403. 1945.
6. Krehl, W. A., Strong, F. M., and Elvehjem, C. A. Ind. Eng. Chem., Anal. Ed. 15 : 471-475. 1943.
7. Lewis, J. R. and Gorham, P. R. Can. J. Research, F, 25 : 133-140. 1947.
8. McIntire, J. M., Schweigert, B. S., Henderson, L. M., and Elvehjem, C. A. J. Nutrition, 25 : 143-152. 1943.
9. McIntire, J. M., Schweigert, B. S., Herbst, E. J., and Elvehjem, C. A. J. Nutrition, 28 : 35-40. 1944.
10. Pyke, M. J. Soc. Chem. Ind. Trans. 58 : 338-340. 1939.
11. Reedman, E. J. and Young, G. A. Can. J. Research, C, 21 : 145-150. 1943.
12. Rice, E. E. and Beuk, J. F. Food Research, 10 : 99-107. 1945.
13. Rice, E. E., Daly, M. E., Beuk, J. F., and Robinson, H. E. Arch. Biochem. 7 : 239-246. 1945.
14. Rice, E. E., Fried, J. F., and Hess, W. R. Food Research, 11 : 305-312. 1946.
15. Sarett, H. P. and Cheldelin, V. H. J. Nutrition, 30 : 25-30. 1945.
16. Schweigert, B. S., McIntire, J. M., and Elvehjem, C. A. J. Nutrition, 26 : 73-80. 1943.
17. Schweigert, B. S., McIntire, J. M., and Elvehjem, C. A. J. Nutrition, 27 : 419-424. 1944.

APPARATUS FOR MEASURING OXYGEN CONSUMPTION OF GUINEA PIGS[1]

By Florence A. Farmer[2] and E. W. Crampton[3]

Abstract

A modification of the Teitelbaum and Harne apparatus for measuring oxygen consumption in guinea pigs has been described. Typical results are given to illustrate the usefulness of the apparatus.

Many types of apparatus have been used to record the oxygen consumption or carbon dioxide production, or both, of animals, as an indirect method for determining their metabolic rate.

The apparatus to be described in this paper (Fig. 1) is a modification of the one designed by Teitelbaum and Harne (1) in which water is drawn into a burette to replace oxygen consumed by the animal.

In any apparatus used for measuring oxygen consumption, a chamber is needed that can be easily opened to admit the animal, readily made airtight again, and conveniently cleaned between each test run. A 10-in. desiccator has proved satisfactory for this purpose. The soda lime is held around the side wall of the desiccator in a removable two-walled container of screening, which rests on a perforated floor. The desiccator can thus be cleaned after each run, without necessarily changing the soda lime. The desiccator is sealed with high vacuum stopcock grease. Lanoline works well but is objectionably sticky. Vaseline cannot be used.

Since it is possible to watch the activity of the animal through the glass top, the respiration rate can be counted while the test is in progress.

The graduated dispensing burette is simple to operate since the level of water can be read off directly and then the burette emptied ready for the next run, without disturbing its position.

Water is maintained in the siphon at all times, regardless of changes in pressure within the burette, by means of the test tube and constant leveling device.

Results

This apparatus has been in continuous use in this laboratory for eight months during which time approximately 500 tests have been run on 50 animals. Some typical results are recorded below.

[1] *Manuscript received August 19, 1947.*

Contribution from the Department of Nutrition, Faculty of Agriculture (McGill University), Macdonald College, Que. Journal Series No. 236.

[2] *Formerly Graduate Assistant, Department of Nutrition.*

[3] *Professor of Nutrition.*

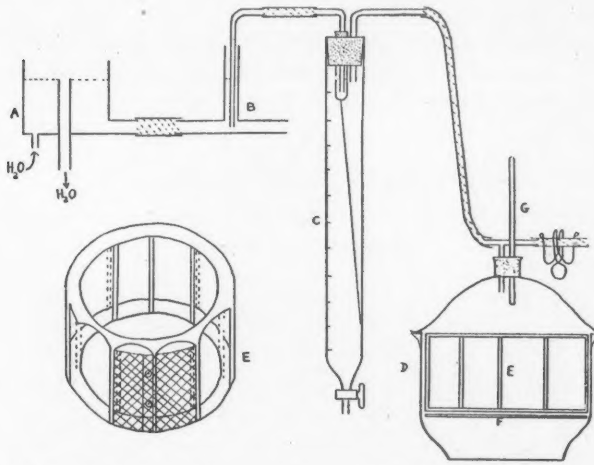

FIG. 1. ***Apparatus for measuring oxygen consumption of guinea pigs.***

A. A water leveling device made of chromium plated brass.

B. A 'T' tube joined to *A* by rubber tubing. There are four in the series, each unit capable of working alone or with the others.

C. A 1000 cc. dispensing burette fitted with a rubber stopper. Hung from the stopper is a test tube with a hole in it. The glass tubing (siphon from *B*) is below the level of the hole, so that the siphon can be maintained. The height of the burette is adjusted until the hole is at the level of the water in the 'T' tube (*B*). Thus no water flows into the burette unless the air pressure is reduced. The string hanging from the test tube prevents splashing.

D. A desiccator fitted with a rubber stopper. A 'T' tube not only allows air to pass from the burette *C* into *D*, as the pressure in *D* drops, but also permits the operator to suck the air out of *D* to start the siphon from *B* to *C* at the beginning of the test.

E. A two-walled wire basket holding soda lime. A frame of brass (chromium plated) is made of two disks held together by rods. The inner screening is threaded between the two sets of rods and secured permanently. The outer screening (copper) surrounds the outer rods and is fastened with two snaps. It can be removed to change the soda lime. The top disk is cut away between each set of rods, to allow for filling the basket by means of a spoon.

F. A perforated floor (chromium plated brass).

G. A thermometer.

To run the test

1. Turn on the water until the level is constant in *B*.

2. Suck on 'T' tube in *D* until the water rises in *B* and siphons over into the test tube in *C*. Continue sucking until water reaches some mark in *C* to be used as starting level.

3. Remove lid from desiccator and put guinea pig in. Replace lid and seal. Seal all other joints with stopcock grease if necessary.

4. Seal off the 'T' tube in *D* with a pinchcock.

5. The test is continued until a given amount of water (300 cc. or 500 cc.) has been drawn over.

Caution

All connections must be airtight.

Uniformity of Response

Table I shows the oxygen consumption of a guinea pig determined daily for 15 days. As would be expected, the day to day variability decreases as the animal becomes accustomed to the apparatus.

TABLE I

OXYGEN CONSUMPTION ON SUCCESSIVE DAYS

Date	Oxygen, ml./min.	Date	Oxygen, ml./min.
Jan. 25	8.8	Feb. 4	10.7
26	10.1	5	10.4
27	9.8	6	11.5
28	11.1	7	10.5
29	8.8	8	10.3
31	9.9	10	10.8
Feb. 1	10.6	11	10.6
3	11.5		

Oxygen Versus Air

The test can be run until such time as the oxygen of the air in the apparatus has been used up. There is no advantage in using pure oxygen in place of air. This is shown by the fact that a pregnant guinea pig drew over water equivalent to 13.7 ml. per min. when air filled the apparatus and 14.6 ml. per min. when pure oxygen was used three days later.

Our data indicate that unless the difference between single runs exceeds 15%, the probability ($P = 0.05$) is that the tests are not really different.

Exhaustion of Soda Lime

The rate at which carbon dioxide is absorbed on the soda lime depends upon the concentration of carbon dioxide in the apparatus and the quantity of soda lime present. Indicator soda lime (450 gm.) is used in each desiccator. Since some animals produce carbon dioxide at a greater rate than others, all tests have been run until a fixed amount of water (300 ml.) has been drawn over, rather than for a fixed time. In this way, the concentration of carbon dioxide at the end of the run is always the same. Our results show that soda lime can be used until it begins to turn blue. Under the conditions of our procedure, each pound of soda lime will absorb carbon dioxide equivalent to 10 liters of water.

Fasting of Animals Prior to Test

We have not made extensive tests comparing basal with resting metabolism. Because of the fasting necessary, and its effect on live weight changes in animals subjected to repeated tests at weekly intervals, basal metabolism could not be employed in the studies for which this apparatus was designed. However, as a matter of interest a few runs were made to determine the effect of fasting on the variability of the oxygen consumption records.

PLATE I

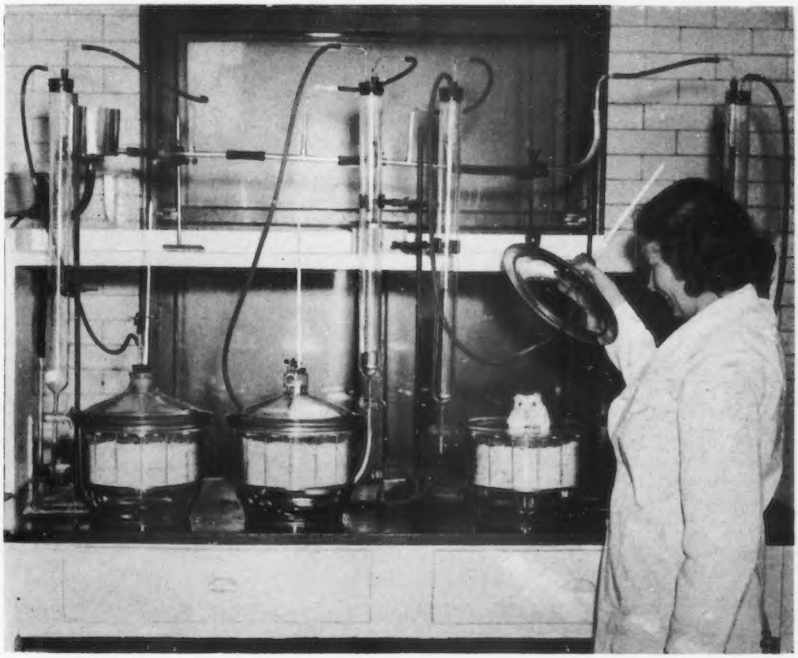

FIG. 2. *Showing actual assembly of apparatus for measuring oxygen consumption of guinea pigs.*

The guinea pigs used for this work were pregnant and on ad libitum feeding. The oxygen consumption of three non-fasted animals was determined on three alternate days. These animals showed a mean oxygen intake of 12.3 ml. per min. and a coefficient of variation of 7.8%. The experiment was then repeated on the same animals, with a 21-hr. fast before each run. This time the average oxygen consumption was lower (10.4 ml. per min.), as would be expected, and the coefficient of variation was 6.2%.

Reference

1. Teitelbaum, H. A. and Harne, O. G. J. Lab. Clin. Med. 26 : 1521-1524. 1941.

THE REDUCING SUGAR CONTENT OF FROZEN EGG AS AN INDEX OF THE BACTERIAL CONTENT[1]

By C. K. Johns[2]

Abstract

Reducing sugar determinations have been proposed as an over-all measure of both bacteriological and chemical changes in frozen egg. When applied to commercial products, the technique recommended has been found to yield poorly reproducible results, while reducing sugar readings show no correlation with viable or microscopic counts of bacteria. Few of the bacteria isolated from commercial melange were able to ferment glucose.

In assessing the quality of frozen egg, the bacterial content deserves consideration, since a high count usually denotes either low grade breaking stock or faulty plant operations. Furthermore, a high count product may spoil during defrosting, while conditions that allow considerable bacterial growth may permit the multiplication of pathogenic types, with a consequent possible public health hazard (2, 3, 4, 7, 10, 11, 12).

However, quality in frozen egg includes other aspects in addition to the bacterial. The type of breaking stock, or the growth of bacteria in the melange, may be reflected in chemical changes, some of which give rise to undesirable flavors and odors in the product. Consequently, various chemical tests have been suggested (6). Among these is the determination of the reducing sugar content. This test has recently been advocated as an over-all indication of egg quality by Pearce and Reid (8), who report that reducing sugar values decreased with increasing numbers of bacteria. Such a test, giving promise of indicating both chemical and bacteriological aspects of egg quality, would be extremely useful in the regulatory control of frozen egg.

It is generally recognized, however, that the bacterial content of a food product has to be well up in the millions per gram before the effect of bacterial activity can be measured by ordinary chemical tests. Consequently, there was reason to doubt the effectiveness of the reducing sugar test as a means of measuring or reflecting the bacterial content. With this in mind, studies were undertaken to determine the degree of correlation between bacterial content and reducing sugar content of commercial frozen egg, and also between each of these measures and plant conditions and operations as observed at the time of sampling. However, since only a few plants were operating when the frozen material was sampled, such observations were obviously of limited value.

[1] *Manuscript received June 19, 1947.*

Contribution No. 240 (Journal Series) from the Division of Bacteriology and Dairy Research, Science Service, Department of Agriculture, Ottawa. Issued as paper No. 198 of the Canadian Committee on Food Preservation.

[2] *Bacteriologist.*

Materials and Methods

During October and November, 1946, Mr. D. A. Fletcher of the Poultry Products Marketing Service, Department of Agriculture, visited a number of plants between Ottawa and the Pacific coast where eggs were broken and frozen for the domestic trade. At each plant, cores of whole egg, white, and yolk were bored, using a sterile 1 in. corer and an electric drill. One portion of the core was placed in a sterile stoppered 7/8 in. × 6 in. Pyrex test tube and kept frozen. When all samples from any city had been collected, they were carefully packed in dry ice and shipped by air express to Ottawa. Here they were rapidly thawed in a water bath and analyzed for (*a*) total viable count on standard milk agar at 32° C. for three days, (*b*) direct microscopic count, and (*c*) coliform count on Bacto violet red bile agar at 37° C. (1). A second portion of each sample was analyzed by Mr. Fletcher in the field for reducing sugars and total solids, using for the former the method employed by Pearce and Reid (8). An additional determination of reducing sugar was made by the Division of Chemistry, Science Service, on the portion of sample remaining after bacteriological analysis, in order to establish reproducibility of results between two workers using the same reagents, etc.

Results

Fig. 1 shows data obtained from 59 samples of frozen whole egg. The lack of correlation is obvious. The majority of samples with viable counts below 1,000,000 per ml. were below the minimum of 300 mgm. %* reducing sugar that had been suggested for Grade A whole egg, while a number of those with very high counts were well above this limit.

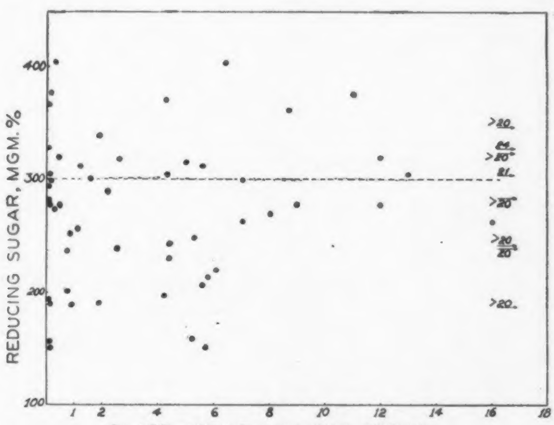

FIG. 1. *Reducing sugar content vs. plate count of 59 samples of commercial frozen whole egg.*

**This represents the number of milligrams in 100 gm., or the percentage ×1000.*

Fig. 2 shows similar data obtained from frozen yolk and white. Again, the lack of correlation is obvious.

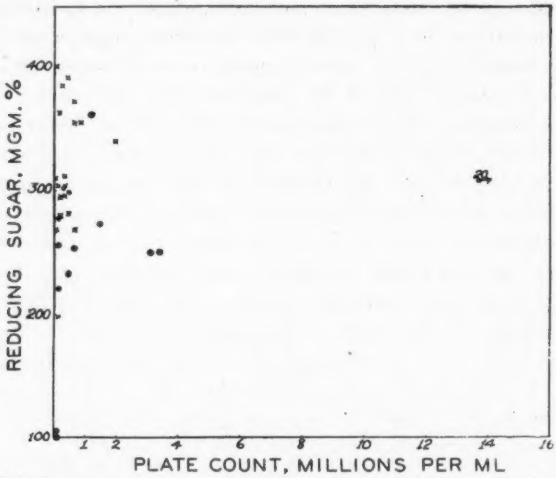

FIG. 2. *Reducing sugar content vs. plate count of commercial frozen yolk (14 samples) and white (20 samples).* ● *= yolk;* × *= white.*

In Figs. 1 and 2 the reducing sugar values are those determined by Mr. Fletcher. The poor agreement between these values and those obtained by the Division of Chemistry is evident from the data in Fig. 3. In general,

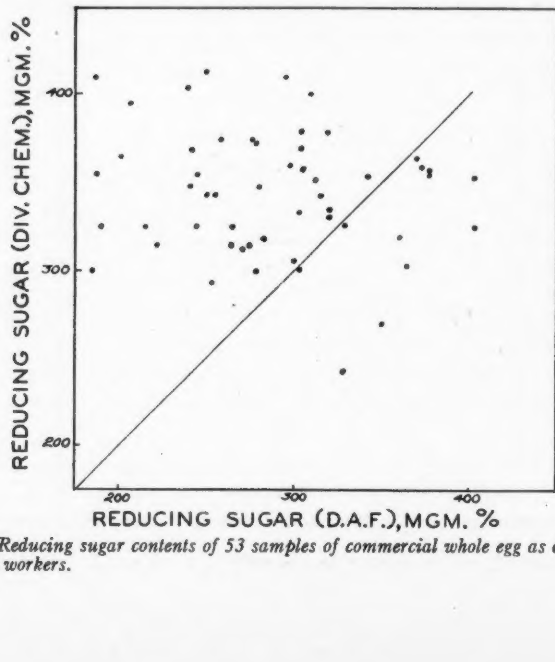

FIG. 3. *Reducing sugar contents of 53 samples of commercial whole egg as determined by two different workers.*

each of the two analysts obtained reasonably satisfactory agreement between their own duplicate determinations. However, subsequent studies, in which the same two workers made parallel determinations in the same laboratory, failed to yield results in close enough agreement to warrant the use of this test in its present form.

The results of an attempt to relate plant conditions and practices to reducing sugar and bacterial contents appear in Table 1. While the reducing sugar

TABLE I

RELATION BETWEEN QUALITY OF BREAKING STOCK, PLANT CONDITIONS AND PRACTICES, ETC., AND BACTERIOLOGICAL AND CHEMICAL DATA

Sample No.	Reducing sugars, mgm. %		Viable count per ml.	Microscopic count per ml.	Coliform count per ml.
	D.A.F.	Div. Chem.			
A. Eggs broken and frozen under ideal conditions					
31	370	364	75,000	—	<100
32	342	353	1,900,000	5,600,000	<100
93	403	330	6,400,000	3,700,000	51,000
94	377	355	11,000,000	3,200,000	30,000
B. Melange produced under sanitary conditions but lacking facilities for fast freezing					
86	222	315	6,000,000	7,900,000	400
87	215	325	5,800,000	9,200,000	<100
88	258	375	1,100,000	3,200,000	78,000
89	239	403	760,000	1,800,000	13,000
90	207	395	5,600,000	6,300,000	38,000
91	193	465	60,000	—	14,000
92	190	325	1,900,000	5,300,000	56,000
C. Melange from candling bench mixed eggs					
1. Placed in good freezer fairly promptly					
70	364	302	8,700,000	12,000,000	400
71	403	354	300,000	3,300,000	<100
74	350	271	>20,000,000	33,000,000	<100
75	298	360	7,000,000	20,000,000	200
2. Placed in poor freezer at end of each day's operations					
54	244	325	>20,000,000	>33,000,000	>100,000
55	242	368	20,000,000	33,000,000	10,000
62	250	—	3,100,000	5,100,000	100
63	273	378	1,500,000	1,900,000	<100

values as determined by Mr. Fletcher appear to correlate well with plant practices and conditions, an inverse relationship exists when the Division of Chemistry values are used. Bacterial counts appear to show little or no

correlation with plant practices. However, it should be pointed out that in most plants such important points as adequacy of sanitizing of utensils and equipment could not be checked, since the sampling was conducted many months after breaking operations had ended.

Discussion

The lack of correlation between bacterial numbers and reducing sugar content found in these studies is not altogether surprising. Even if a close correlation existed between the reducing sugar content and the bacterial content of the egg at the moment of breaking, this might easily be upset by a heavy pick-up of bacteria from equipment. If no opportunity existed for subsequent bacterial growth in the melange before freezing, this would not affect the reducing sugar content. Furthermore, various workers have shown that a high proportion of the bacteria present within the egg are unable to utilize reducing sugars in their growth processes. Finally, there is little published information concerning the effect of climate, season, storage, and other factors upon the reducing sugar content, and little is known as to how widely normal eggs vary in this constituent.

The lack of agreement between our results and those reported by Pearce and Reid (8) concerning the correlation between bacterial numbers and reducing sugar content may arise from the fact that they worked with Grade A eggs, broken out under nearly aseptic conditions in the laboratory, while our samples were obtained from a number of commercial plants breaking and freezing lower grades of eggs. It is probable that sugar-fermenting types, coming from the shells, were more common in their melange; Gillespie (5) has noted that Gram-positive cocci make up a very considerable part of the normal flora of the egg shell, while they occur infrequently in commercial melange. This we had also found to be true in previous studies. For further confirmation, plates from five samples of frozen whole egg in the present studies were selected; from each 50 adjacent colonies were fished onto slants of Difco tryptone glucose extract milk agar (1) containing brom-cresol purple indicator. After incubation at room temperature for two to three days, the slants were examined and any evidence of acid formation recorded. Results were as follows:

Sample No.	Reducing sugar, mgm. %		Viable count per ml.	Acid formers, %
	D.A.F.	Div. Chem.		
42	250	343	5,300,000	< 2
45	373	359	4,300,000	2
52	275	314	280,000	12
54	244	325	>20,000,000	< 2
55	242	368	>20,000,000	< 2

With such small proportions of acid-forming bacteria, a high degree of correlation between reducing sugars and bacterial numbers could scarcely be expected.

Although the data are not shown, direct microscopic counts also showed no better correlation with reducing sugar readings than did viable counts. At first it appeared that the content of coliform organisms might afford a good index to the bacteriological and sanitary quality, but analysis of additional samples revealed many anomalies between coliform content, other bacteriological counts, and reducing sugar content.

In 1921, discussing the proposal to use the reducing sugar content, Redfield (9) remarked: "Whether Todd's general deduction (p. 512), that the dextrose content is a more reliable indication of the age of the eggs than the ammonia nitrogen, is true or not depends entirely upon the bacterial flora of the eggs and whether the predominating changes during aging are fermentative, proteolytic, or lipolytic. Since they may be any of these, the quality of eggs cannot be judged by any one chemical method." Our findings appear to underline the last sentence. While it would be most convenient to have a single chemical test that would indicate over-all quality in frozen egg, in view of the considerations indicated by Redfield, it seems unlikely that one will be found. Apparently, it will be necessary to resort to a combination of bacteriological and chemical examinations, supplementing organoleptic tests, in order to obtain a true picture of the quality of frozen egg products.

Acknowledgments

Thanks are extended to those firms that made available for sampling their stocks of frozen eggs; to Mr. D. A. Fletcher of the Poultry Products Marketing Service, for collecting samples and data, and for making available the results of his reducing sugar determinations; to Mr. J. T. Janson and his staff of the Division of Chemistry, Science Service, Department of Agriculture, Ottawa, for making the additional reducing sugar determinations reported; and to Mr. J. G. Desmarais for technical assistance with the bacteriological tests.

References

1. American Public Health Association. Standard methods for the examination of dairy products. 8th ed. Am. Public Health Assn., New York. 1941.
2. Crowe, M. J. Hyg. 44 : 342-345. 1946.
3. Gibbons, N. E. and Moore, R. L. Can. J. Research, F, 22 : 48-57. 1944.
4. Gibbons, N. E. and Moore, R. L. Can. J. Research, F, 22 : 58-63. 1944.
5. Gillespie, J.M. J. Council Sci. Ind. Research, 19 : 117-127. 1946.
6. Lepper, H. A., Bartram, M. T., and Hillig, F. J. Assoc. Official Agr. Chem. 27 : 204-223. 1944.
7. Mitchell, R. B., Garlock, F. C., and Broh-Kahn, R. H. J. Infectious Diseases, 79 : 57-62. 1946.
8. Pearce, J. A. and Reid, M. Can. J. Research, F, 24 : 437-444. 1946.
9. Redfield, H. W. J. Assoc. Official Agr. Chem. 4 : 516-520. 1921.
10. Schneider, M. D. Food Research, 11 : 313-318. 1946.
11. Solowey, M., Spaulding, E. H., and Goresline, H. E. Food Research, 11 : 380-390. 1946.
12. Watt, J. Public Health Repts. 60 : 835-839. 1945.

THE RESISTANCE TO WEATHERING OF COTTON DUCK TREATED WITH CERTAIN COMPOUNDS OF IRON, CHROMIUM, AND COPPER[1]

By Muriel W. Weatherburn[2] and C. H. Bayley[2]

Abstract

Unbleached cotton tentage duck was impregnated with chromic oxide, copper carbonate, and ferric oxide, both singly and in mixtures, each metal being present in concentration of approximately 1% as metallic oxide, and also in the form of naphthenates in equivalent concentration. The rot resistance of the treated samples was determined by measuring the loss of breaking strength on soil burial after leaching in water and after outdoor weathering for four months. Photochemical degradation on weathering was determined by measuring the loss of breaking strength and increase in cuprammonium fluidity. The decrease in metal content on weathering was also measured.

Samples treated with chromium and iron in inorganic form, used singly and together, showed no resistance to soil burial and very slight resistance when the metals were present as naphthenates. All treatments containing copper produced substantial resistance to soil burial, the mixtures producing greater resistance than the single compounds; the resistance resulting from treatment with chromium plus copper and with chromium plus copper plus iron mixtures was greater than that from the corresponding copper plus iron treatments. On the whole, the inorganic treatments produced more resistance to soil burial after leaching than the organic treatments but, after weathering, the copper alone and copper plus iron treatments produced less resistance than the corresponding naphthenate treatments.

All the inorganic treatments containing chromium exerted a marked protective effect against deterioration resulting from weathering as judged by breaking strength losses and increases in cuprammonium fluidity.

The naphthenate treatments containing chromium and the iron oxide and iron naphthenate treatments afforded some protection with respect to breaking strength loss but produced fluidity increases approximately the same as that of the untreated fabric. Similar results were obtained with the copper carbonate plus iron oxide treatment.

The samples treated with copper carbonate and copper naphthenate showed breaking strength losses approximately the same as that of the untreated control but gave evidence of enhanced degradation as judged by the fluidity data.

Losses of chromium on weathering were negligible in all cases while losses of iron ranged from zero to 34%. Complete loss of copper occurred in the copper carbonate treated sample and a slightly lower loss (85%) in the copper plus iron treated sample. In the presence of chromium and chromium plus iron, the losses of copper were reduced to 34% and 54% respectively. Similar trends were observed with the naphthenate treatments but the losses were much lower in all cases, ranging from no significant loss to a loss of 48%.

Treatments involving the application of chromium, iron, or copper in various inorganic forms have long been used for the protection of cellulosic fabrics from microbiological attack. Thus for example a treatment usually referred to as 'mineral khaki' or 'mineral dye' has been used widely throughout the British Empire for the protection of such fabrics as tentage ducks. In this process the fabric is treated with a solution of chromium and iron salts and the treatment is subsequently 'developed' by passage of the fabric through an

[1] *Manuscript received May 23, 1947.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1659.

[2] *Chemist.*

alkaline bath containing sodium hydroxide and sodium carbonate, or both, the fabric being subsequently washed with water and dried. The chromium and iron fixed on the fabric in this process are present as hydrated oxide, the metals being in trivalent form. The treatment appears to impart considerable protection against the actinic degradation that normally occurs in cotton fabrics on exposure to outdoor weathering (2, 9, 15) and against similar degradation occurring during accelerated weathering (8). This protection seems to be largely related to the presence of the chromium oxide, which by itself shows a high degree of resistance to weathering (9, 15). Provided that the amount of chromium oxide (Cr_2O_3) does not fall below approximately 0.75% based on the weight of the fabric, the mineral khaki treatment imparts some resistance to mildew, but provides little or no resistance to severe microbiological attack such as occurs through the action of the bacterial flora of normal soil or decaying vegetation under suitable conditions of temperature and humidity (2, 5, 22). In this connection it is of interest to note that a recent Australian report indicates that deterioration of mineral khaki treated cotton tentage duck may result from the accumulation of decaying leaves, etc. on the surface of the fabric. Thaysen and Bunker (26) in summarizing the shortcomings of chromium oxide – iron oxide treatments have stated that such treatments "afford appreciable protection against microbiological decay but cannot claim to ensure permanent protection. Where material is not likely to suffer exposure in soil, in water, or under conditions of excessive dampness, the treatment may be employed until such time as a more effective treatment has been devised."

An interesting modification of the 'mineral dye' process consists in replacing the alkaline developing bath with an aqueous solution of potassium chromate. In this process the chromium is precipitated in the form of a chromium chromate to which the formula $3Cr_2O_3.4CrO_3$ has been assigned by Race and co-workers (16). These investigators have shown that chromium in hexavalent form is the only constituent of the chromium–iron treatment that confers rot resistance, and that this chromium chromate is hydrolyzed in the washing process to yield pigments in which the ratio of trivalent to hexavalent chromium increases with time of washing until the hexavalent chromium is completely decomposed. Moreover, these workers have shown that during the washing process some chemical deterioration of the cotton may take place through the action of the chromic acid produced in the hydrolysis. The iron chromate precipitated in the chromate development appears to be more readily hydrolyzed than the corresponding chromium chromate referred to above, and can likewise produce chemical deterioration of the cotton yarn with which it is in contact. Further extensive studies on the properties of the pigments produced by the two types of development and the factors affecting their formation have been made by Race and co-workers (17–21). It has also been found by Race *et al.* (22) that outdoor weathering had a pronounced effect in bringing about hydrolysis of hexavalent chromium.

Data on the behavior of fabrics subjected to iron treatments alone are meagre. Jarrell *et al.* (13) reported that the presence of ferric oxide accelerated chemical degradation occurring during weathering, while Cunliffe *et al.* (8) have stated that such treatments exert a slight protective action toward the effects of weathering. The resistance to microbiological attack afforded by such treatments appears to be negligible.

Copper carbonate treatments have been reported to cause enhanced actinic degradation on weathering and to be readily removed by leaching during weathering (9, 13, 24). Such treatments provide good resistance to microbiological attack for such time as the copper remains in the fabric (6, 10, 11).

The mixture of copper carbonate and iron oxide in cotton yarns and fabrics has been extensively investigated by Race and co-workers who claim that such treatments produce a high degree of resistance to microbiological attack, and also that in such mixtures copper is not as readily removed by water leaching as with the copper carbonate treatment alone. The extent of actinic degradation in several experiments was the same as that of the untreated fabric (2, 5, 15). These data have been challenged by other investigators who claim that the presence of copper in such treatments causes an acceleration of actinic degradation. It was also reported by Race that yarn treated with a mixture of chromium oxide and copper carbonate containing approximately 1% of each metal as oxide showed the same rate of removal of copper by leaching in running water at pH 5.3 to 5.5 as that of yarn treated with copper carbonate alone (23).

In investigating the properties of the copper–iron treatment, Race *et al.* found that incorporation of chromium with the copper and iron salts did not affect the rot resistance as judged by filter candle tests using horse dung inoculum (23). In a copper–chromium–iron treatment the protective value of chromium on weathering was destroyed by the presence of copper (15) although it should be pointed out that the concentration of chromium in this experiment was rather low, 0.39% chromic oxide.

Other work (2) has shown that the after treatment of a typical mineral khaki treated duck with copper naphthenate applied from solvent greatly improved the rot resistance of the mineral khaki treated fabric and did not appear to increase the extent of actinic degradation. Moreover, the loss of copper by leaching during weathering was less than that occurring in a similar fabric treated with copper naphthenate alone.

In view of the conflicting data pertaining to treatments with chromium, copper, and iron referred to above, it was of interest to study the rotproofing efficacy and weathering characteristics of chromium, copper, and iron salts incorporated in cotton duck by alkali precipitation. The metals were used singly, in concentration of approximately 1% expressed as the metallic oxides, and also in binary and ternary mixtures in order to study the interactive effects of the metals in mixture. Investigation was also made of the behavior of these metals when applied to the fabric in similar concentrations from solvent solution in the form of naphthenates.

Materials and Treatments

The cotton fabric was an unbleached army duck weighing 10 oz. per square yard and having 46 three-ply warp and 37 two-ply weft yarns per inch. The chemicals were of technical grade.

All treatments were carried out in the laboratory. The inorganic treatments were applied by a two-bath method in which a loop of fabric was impregnated with a soluble salt of the metal by continuous passage through a laboratory padder followed by similar passage through a solution of sodium carbonate. A complete description of the method of sampling and treatment by aqueous procedure has been given in a previous paper (2). The concentrations of the treating solutions in the present experiment were as follows:

Bath (1) Chromium impregnation—chromic sulphate ($Cr_2(SO_4)_3 \cdot 18H_2O$), 120 gm. per liter
Copper impregnation— copper sulphate ($CuSO_4 \cdot 5H_2O$), 50 gm. per liter
Iron impregnation— ferric ammonium sulphate ($Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$), 67 gm. per liter

For precipitation of mixtures of the compounds, the concentrations of the copper and iron salts were increased to 87 and 93 gm. per liter respectively. Impregnation for 15 min. at 71° C.

Bath (2) Impregnation for 10 min. at 49° C. in a solution of anhydrous sodium carbonate, 50 gm. per liter. The treated fabric was washed for two hours in running tap water.

The naphthenate treatments were applied from solution in Stoddard solvent as previously described (4). The percentage of metal applied in these treatments is expressed in terms of metallic oxides in order to conform with the method of expressing the metallic content of the inorganic treatments.

The colors of the treated fabrics were as follows:

Metal	Inorganic treatments	Naphthenate treatments
Chromium	Medium blue gray	Medium gray with mauve tint
Copper	Medium blue green	Medium blue green
Iron	Medium orange tan	Light tan
Chromium + copper	Medium blue green	Medium blue gray
Chromium + iron	Grayish tan	Medium tan with mauve tint
Copper + iron	Deep tan	Medium grayish green
Chromium + copper + iron	Olive green	Dark gray with greenish tint

Test Methods

The sampling procedure was the same as that used previously (2), each breaking strength value being obtained from 10 breaks, using duplicate sets of five breaks each.

For outdoor weathering the samples were attached to frames as described previously (2) and were exposed on the roof of the National Research Laboratories, Ottawa, from May 1 to Aug. 31, 1946, a period of four months.

The methods used for the determination of breaking strength, soil burial, leaching, and cuprammonium fluidity were those given in Schedule 4-GP-2-1944, *Methods of Testing Textiles*, of the Canadian Government Purchasing Standards Committee. Of the metal concentrations, copper when used alone was determined by the ignition method (7); copper and iron together were determined by the method of Race (15); and other metals, used singly and in combination, were determined by the methods of the Textile Institute of Great Britain (25); the two latter methods were used with slight modifications as described previously (2).

Data

Weather Conditions

Data for rainfall and hours of sunshine during the exposure period are given in Table I. The total hours of sunshine were similar to those during the 1944 (1) and 1945 (2) exposures, and the amount of rainfall was approximately the same as for the 1945 exposure but greater than the 1944 exposure. None of the weathered samples showed evidence of significant mildew growth.

TABLE I
WEATHER CONDITIONS DURING EXPOSURE OF SAMPLES

Period	Mean daily temp., °F.		Rainfall, in.	Bright sunshine, total hours
	Maximum	Minimum		
May 1 to May 4	57	37	0.20	49.5
5 11	57	37	0.54	40.1
12 18	65	44	1.55	51.3
19 25	66	48	0.38	40.4
26 to June 1	68	47	0.23	54.6
June 2 to June 8	71	48	0.71	36.6
9 15	68	46	0.61	78.3
16 22	74	51	3.49	62.3
23 29	91	62	0	83.7
30 to July 6	81	62	0.37	87.9
July 7 to July 13	80	58	0.88	75.5
14 20	86	55	0.04	71.2
21 27	82	59	1.57	46.3
28 to Aug. 3	86	57	0.44	51.8
Aug. 4 to Aug. 10	91	59	2.25	67.1
11 17	79	62	0.11	46.4
18 24	77	52	1.10	26.5
25 31	77	48	0.44	38.4
Average	77	52		
Total			14.91	1007.9

Breaking Strength Loss

Breaking strength data are given in Table II.

Statistical analysis showed that breaks occurring at the jaws of the machine gave lower and somewhat more erratic values than those occurring at some

TABLE II

EFFECT OF WEATHERING AND BURIAL ON BREAKING STRENGTH

—	Breaking strength, lb.						Breaking strength loss, %				
	Orig. leached	Weath. 4 months	Buried for two weeks after		Buried for four weeks after		Weath. 4 months	Buried for two weeks after		Buried for four weeks after	
			Leach. 24 hr.	Weath. 4 months	Leach. 24 hr.	Weath. 4 months		Leach. 24 hr.	Weath. 4 months	Leach. 24 hr.	Weath. 4 months
Inorganic treatments											
Chromium	189(7)	139(7)	0	10(9)	0	0	26	100	95	100	100
Copper	181(10)	89(8)	158(7)	37(8)	48(10)	5(10)	51	13	79	73	97
Iron	184(8)	132(8)	0	20(10)	0	0	28	100	89	100	100
Chromium + copper	178(6)	176(10)	187(7)	169(6)	104(10)	142(5)	1	+5	5	42	22
Chromium + iron	195(6)	161(6)	0	15(9)	0	0	17	100	92	100	100
Copper + iron	181(6)	128(9)	189(9)	116(6)	133(9)	47(8)	29	+4	36	27	74
Chromium + copper + iron	190(6)	161(7)	206(8)	164(9)	163(9)	136(5)	15	+8	14	14	28
Naphthenate treatments											
Chromium	211(9)	127(7)	22(10)	40(10)	13(10)	0	40	89	81	94	100
Copper	202(9)	99(9)	95(9)	98(8)	19(10)	93(10)	51	53	51	91	54
Iron	207(9)	123(8)	38(9)	53(8)	14(10)	0	41	82	75	93	100
Chromium + copper	220(9)	143(10)	132(8)	141(5)	32(10)	128(4)	35	40	36	85	42
Chromium + iron	217(8)	136(6)	66(8)	52(9)	50(8)	0	37	70	76	77	100
Copper + iron	211(8)	113(7)	137(10)	111(7)	37(9)	103(8)	46	35	47	82	46
Chromium + copper + iron	211(9)	152(6)	176(9)	155(7)	74(9)	142(9)	28	17	27	65	33
Untreated control	183(9)	94(7)	0	24(10)	0	0	49	100	87	100	100

NOTE: *Figures in parentheses represent the number of 'good' breaks on which the average was based, jaw breaks being discarded.*

distance from the jaws; consequently the 'jaw breaks' were not included in the breaking strength averages. Subsequently in this paper the accepted breaks will be designated as 'good' breaks.

For statistical significance at the 5% level, on averages of 10 good breaks, the necessary differences are as follows: leached samples 17 lb., weathered samples 10 lb., leached and buried samples 21 lb., weathered and buried samples 16 lb. In those cases in which 10 good breaks were not obtained, owing to jaw breaks, a formula described elsewhere (12) was used to test for the significance of differences between certain samples. The percentage losses of breaking strength, as given in Table II, were based on the strengths of the leached original samples. It should be borne in mind that the breaking strength data obtained in this way may be somewhat misleading unless due regard is given to the fact that the naphthenate solutions caused a marked increase in the strength of the original fabric whereas the aqueous procedures had no effect.

Weathering Effects

After outdoor weathering the strength of the copper carbonate treated sample was the same as that of the untreated sample, whereas the strengths of all the other inorganic treated samples were considerably higher than the untreated. Of this latter group the strengths of the samples containing iron alone and copper plus iron were similar, and were less than the strengths of the samples containing chromium plus copper, chromium plus iron, and chromium plus copper plus iron.

Similar relations between the breaking strengths were shown by the samples treated with metallic naphthenates. In this set the difference between the strength of the copper–iron treated sample (113 lb.) and the copper treated sample (99 lb.) is not as great as with the inorganic treatments, but nevertheless the difference is significant since the necessary difference from calculation was found to be 10.7 lb.

Comparing the inorganic and the naphthenate applications, it is apparent that the samples containing copper alone, iron alone, and chromium plus copper plus iron were similar in strength but in all other cases the inorganic treated samples were stronger than the corresponding naphthenate treated samples.

Burial Effects

All samples containing copper showed considerable resistance to burial for two weeks with preliminary leaching, the resistance provided by the copper naphthenate used alone being lower than that provided by the other copper treatments, and the resistance of the naphthenate treatments containing copper being lower than that of the corresponding inorganic treatments. Inorganic treatments of iron and chromium used singly or in combination offered no resistance to soil burial whereas the corresponding naphthenates offered some slight resistance. The superiority of the inorganic mixtures containing copper over the naphthenates was more noticeable after burial for

four weeks with preliminary leaching, although the strength of the sample treated with copper carbonate alone was reduced considerably. The inorganic treatments containing copper plus iron and copper plus chromium were somewhat less effective than the ternary combination, although both of these treatments were more effective than the ternary combination of naphthenates after burial for four weeks. The most effective treatment in soil burial tests was the inorganic combination of chromium plus copper plus iron.

Weathering Followed by Burial

Burial for two weeks after outdoor weathering produced a substantial loss of strength beyond that produced by weathering alone in the case of the chromium and iron treatments, used singly and in combination, both in inorganic and in naphthenate form, and in the case of the copper carbonate used singly. With all other treatments, i.e., copper naphthenate used singly and all binary and ternary mixtures containing copper, there was no significant change of strength on burial for two weeks after weathering. Four weeks' burial caused a substantial decrease in the strength of the fabric treated with copper plus iron inorganic treatment and a slight decrease in the strength of the fabric treated with copper plus chromium and copper plus chromium plus iron inorganic treatment, but did not affect appreciably the strengths of samples treated with copper-containing naphthenate.

Loss of Metal

The data in Table III show that chromium in inorganic form and in the

TABLE III

LOSS OF TREATING COMPOUND ON WEATHERING

——	Metal, %[a]						Loss of metal, %		
	Original			Weathered					
	Chromium	Copper	Iron	Chromium	Copper	Iron	Chromium	Copper	Iron
Inorganic treatments									
Chromium	0.98			0.96			2.0		
Copper		0.89			0			100	
Iron			1.23			1.23			0
Chromium + copper	1.00	0.97		0.93	0.64		7.0	34.0	
Chromium + iron	1.00		0.80	0.93		0.66	7.0		17.5
Copper + iron		1.03	1.11		0.15	0.99		85.4	1.1
Chromium + copper + iron	0.72	0.96	0.97	0.69	0.44	0.64	4.2	54.2	34.0
Naphthenate treatments									
Chromium	0.91			0.93			+2.2		
Copper		0.86			0.45			47.7	
Iron			0.90			0.89			1.1
Chromium + copper	0.89	0.90		0.93	0.80		+4.5	1.1	
Chromium + iron	0.80		1.05	0.86		0.82	+7.5		21.9
Copper + iron		0.89	0.88		0.56	0.93		37.1	+5.7
Chromium + copper + iron	0.77	0.92	1.26	0.82	0.87	0.89	+6.5	5.4	29.4

[a] *Expressed as Cr_2O_3, Fe_2O_3, and CuO respectively.*

form of naphthenate, both alone and in mixtures, imparted a high degree of resistance to weathering. Iron alone and with copper, both in inorganic form and in the form of naphthenate, imparted a high degree of resistance to weathering but was removed to a moderate extent from the fabrics treated with chromium plus iron plus copper and to a lesser extent from those treated with chromium plus iron. Copper carbonate used alone was completely removed by weathering, and when used with iron oxide produced slight resistance, the loss of copper being 85.4%. The fabrics treated with chromium plus copper and chromium plus iron plus copper inorganic treatment were markedly more resistant to loss of copper. In the naphthenate treated fabrics the copper losses showed the same general trend as in those treated with inorganic copper, but the losses were much less severe.

Cuprammonium Fluidity

None of the treating procedures caused any chemical degradation of the original fabric, as shown by the cuprammonium fluidity data in Table IV.

TABLE IV

EFFECT OF WEATHERING ON CUPRAMMONIUM FLUIDITY

—	Cuprammonium fluidity (reciprocal poises)		
	Original	Weathered	Increase on weathering
Inorganic treatments			
Chromium	3.6	10.7	7.1
Copper	3.5	23.4	19.9
Iron	2.9	15.1	12.2
Chromium + copper	2.2	7.7	5.5
Chromium + iron	2.4	7.4	5.0
Copper + iron	3.0	16.1	13.1
Chromium + copper + iron	2.8	9.1	6.3
Naphthenate treatments			
Chromium	3.3	18.9	15.6
Copper	2.8	21.8	19.0
Iron	2.8	17.4	14.6
Chromium + copper	3.4	17.2	13.8
Chromium + iron	2.6	14.9	12.3
Copper + iron	3.0	21.9	18.9
Chromium + copper + iron	3.0	16.8	13.8
Untreated control	3.1	16.9	13.8

With the inorganic treatments, the presence of chromium seemed to give considerable protection against actinic degradation, the fluidity increases of all samples containing chromium being lower than that of the untreated control. The samples subjected to naphthenate treatments containing chromium showed fluidity increases approximately the same as that of the untreated

control. Copper carbonate used alone, and the naphthenates of copper used alone and copper plus iron, produced fluidity increases that were greater than that of the untreated fabric. Samples treated with iron oxide, iron naphthenate, and iron oxide plus copper carbonate showed fluidity increases similar to that of the untreated fabric.

Discussion of Data

These data have confirmed the findings of other investigators and the results of previous work carried out in these laboratories with respect to the properties of treatment with chromium oxide applied singly and in combination with iron oxide. These treatments have been shown to have good permanence to weathering and to provide marked protection against actinic degradation but to impart no resistance to microbiological attack of the type produced by soil organisms. Iron oxide was found to have a considerable degree of permanence but to be without any effect on actinic degradation and to provide no resistance to microbiological attack.

The data also confirm previous observations that copper in the form of copper carbonate, while effective as a rotproofer, is readily removed by weathering and tends to increase the extent of actinic degradation.

The addition of iron oxide to the copper carbonate increased the rot resistance and decreased the photochemical degradation produced by the copper carbonate, although the loss of copper on weathering was only slightly lower than the loss from copper carbonate alone. The breaking strength of the fabric containing inorganic copper–iron was slightly greater than, and the rise in its fluidity the same as, that of the untreated fabric.

The addition of chromium oxide to copper carbonate resulted in excellent protection against actinic degradation, as judged by both breaking strength and cuprammonium fluidity, with a substantial reduction of the loss of copper on weathering, as well as a marked improvement in resistance to soil burial. The addition of iron oxide did not affect appreciably the chromium oxide – copper carbonate treatment.

With regard to the naphthenate treatments, it is apparent that chromium and iron possess a high degree of permanence on weathering and impart very considerable resistance to actinic degradation as judged by breaking strength data, but that the resistance as judged by increase in cuprammonium fluidity is much lower than that of the inorganic applications. On the other hand, in naphthenate form, chromium and iron imparted some slight resistance to rotting, whereas in inorganic form they did not produce any measurable resistance. It has been established (8, *) that naphthenic acids impart some rot resistance and it seems possible that these acids might also be responsible for some chemical degradation on exposure to weather. This latter factor is receiving further investigation.

* *Unpublished data, N.R.C.*

Copper naphthenate treated samples showed similar weathering effects to those treated with copper carbonate although the loss of copper was less severe. The lower loss of copper on weathering was probably responsible for the greater resistance of the copper naphthenate treated sample to soil burial after weathering, since the resistance to soil burial after leaching was less than that of the copper carbonate.

The addition of the naphthenates of chromium, iron, or chromium plus iron to copper naphthenate produced effects similar to those of the inorganic treatments, with the exception that the change of cuprammonium fluidity was less pronounced, the increase in fluidity in no case being lower than that of the untreated fabric.

Acknowledgments

The authors wish to express their appreciation to Nuodex Products Inc., Elizabeth, N.J., U.S.A., and to Nuodex Products of Canada Ltd., Leaside, (Toronto), Ont., for providing the supplies of the naphthenates used in this investigation; also to Dr. J. W. Hopkins, Biometrician, Division of Applied Biology, National Research Laboratories, for the statistical analysis of the data; to Mr. F. W. Baker, Meteorological Observer, Central Experimental Farm, Department of Agriculture, Ottawa, for providing weather data; and to Miss E. E. Raphael and Messrs. H. S. Quinn and B. H. Pout for assistance in carrying out the work.

References

1. BAYLEY, C. H. and WEATHERBURN, M. W. Can. J. Research, F, 24 : 193-202. 1946.
2. BAYLEY, C. H. and WEATHERBURN, M. W. Can. J. Research, F, 25 : 92-109. 1947.
3. BAYLEY, C. H. and WEATHERBURN, M. W. Can. J. Research, F, 25 : 209-220. 1947.
4. BAYLEY, C. H. and WEATHERBURN, M. W. Can. Textile J. 62 (March 9) : 34, 36, 46. 1945. *or* Am. Dyestuff Reptr. 34 : 247-248. 1945.
5. BAYLEY, C. H. and WEATHERBURN, M. W. Examination of British rotproofed fabrics. Report to the National Research Council of Canada Co-ordinating Committee on Protective Equipment (Research). Dec. 31, 1945.
6. BERTOLET, E. C. Am. Dyestuff Reptr. 32 : 214-219, 226-227. 1943.
7. BRITISH STANDARDS INSTITUTION. British standard specification (ARP series) for rotproofed jute, hessian sandbags. BS/ARP 57, Brit. Standards Inst., 28 Victoria St., London. Aug. 1941.
8. CUNLIFFE, P. W. and FARROW, F. D. *Appendix by* Cunliffe, P. W. and MIDGLEY, E. J. Textile Inst. 19 : T169-T188. 1928.
9. FARGHER, R. G. J. Soc. Dyers Colourists, 61 : 118-122. 1945.
10. FURRY, M. S. and ROBINSON, H. M. Am. Dyestuff Reptr. 30 : 504, 520-524. 1941.
11. FURRY, M. S., ROBINSON, H. M., and HUMFELD, H. Ind. Eng. Chem. 33 : 538-545.1941.
12. HOPKINS, J. W. and WEATHERBURN, M. W. Can. J. Research, F, 25 : 264-272. 1947.
13. JARRELL, T. D., STUART, L. S., and HOLMAN, H. P. Am. Dyestuff Reptr. 26 : 495-500, 519-523. 1937.
14. MARSH, P. B., GREATHOUSE, G. A., BOLLENBACHER, K., and BUTLER, M. L. Ind. Eng. Chem. 36 : 176-181. 1944.
15. RACE, E. and ROWE, F. M. J. Soc. Dyers Colourists, 62 : 19-29. 1946.
16. RACE, E., ROWE, F. M., and SPEAKMAN, J. B. J. Soc. Dyers Colourists, 57 : 213-223. 1941.
17. RACE, E., ROWE, F. M., and SPEAKMAN, J. B. J. Soc. Dyers Colourists, 57 : 257-264. 1941.

18. RACE, E., ROWE, F. M., and SPEAKMAN, J. B. J. Soc. Dyers Colourists, 58 : 32-36. 1942.
19. RACE, E., ROWE, F. M., and SPEAKMAN, J. B. J. Soc. Dyers Colourists, 58 : 161-162. 1942.
20. RACE, E., ROWE, F. M., and SPEAKMAN, J. B. J. Soc. Dyers Colourists, 61 : 224-233. 1945.
21. RACE, E., ROWE, F. M., and SPEAKMAN, J. B. J. Soc. Dyers Colourists, 61 : 233-236. 1945.
22. RACE, E., ROWE, F. M., and SPEAKMAN, J. B. J. Soc. Dyers Colourists, 61 : 310-321. 1945.
23. RACE, E., ROWE, F. M., and SPEAKMAN, J. B. J. Soc. Dyers Colourists, 62 : 9-19. 1946.
24. STRINGFELLOW, W. A. Am. Dyestuff Reptr. 28 : 388-390. 1939.
25. TEXTILE INSTITUTE OF GREAT BRITAIN. Tentative textile standard No. 10. J. Textile Inst. 35 (9) : S7-S40. 1944.
26. THAYSEN, A. C. and BUNKER, H. J. Report on the iron – chromium treatment for the preservation of fabrics from microbiological destruction. Dept. of Sci. Ind. Research, G. Brit., Fabrics Co-ord. Research Comm. Paper No. A50 (mimeog.). 22 Jan. 1927.

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

II. THE EFFECT OF FLOW CONFIGURATION ON THE VELOCITY OF THE OXIDATION REACTION IN PENTANE-AIR MIXTURES[1]

By R. O. King[2]

Abstract

Reynolds Numbers for the commonly used rates of flow of a reacting mixture through a conventional combustion tube are far below the critical value. The laminar flow to be expected accordingly is disturbed by convection currents when the tube is heated and flow configuration depends on such factors as ratio of length to diameter and temperature gradients but can be varied by creating local differences of flow velocity within a uniformly heated reaction space such as reaction chamber No. 10 described in Part I. The effects on reaction velocity of the factors mentioned have been determined by experiments described in this part. The results indicate that the velocity of a heterogeneous reaction is determined by flow configuration, that 'packing' does not distinguish between homogeneous and heterogeneous reactions and that the oxidation of pentane, taken as a typical hydrocarbon, is a heterogeneous reaction.

Section I

Introduction

It was shown by experiments described in Part I (2) that the dimensions and design of reaction spaces were major factors affecting reaction velocity. These factors determine flow configuration and can be varied to produce laminar or turbulent flow or a mixture of both types.

When gas flow through a tube is laminar, velocity is regarded as zero in the layer adjacent to the surface and as increasing in successive layers to a maximum at the longitudinal axis. The average velocity is directly proportional to pressure difference and the energy required to maintain the flow is expended in overcoming viscosity. Laminar flow breaks down to turbulent motion when the velocity through the tube reaches the critical value of the Reynolds Number. Turbulent motion tends to fill the tube and velocity becomes nearly uniform over a cross section normal to the longitudinal axis and is proportional to the square root of pressure difference. The energy required to maintain the flow increases accordingly and is expended in large part in overcoming friction between the wall and the gas stream. The friction gives rise necessarily to a scouring effect.

The flow configuration in an unheated combustion tube can now be considered. A glass tube 2.31 cm. internal diameter was used for many oxidation experiments, air being supplied at the rate of 100 cc. per min. The average velocity is then 0.4 cm. per. sec. and the Reynolds Number 6.58. The critical value for ordinary glass tubing is about 2300 in any self-consistent system of units, thus it would be necessary to increase the air supply in the ratio

[1] *Manuscript received June 24, 1947.*
Contribution from Defence Research Board, Ottawa, Canada.

[2] *Research Scientist, Naval Division, Defence Research Board; lately Director of Scientific Research and Development, Royal Canadian Navy.*

2300/6.58, that is, to about 3500 cc. per min. to initiate what is generally described as turbulence. It would be difficult though not impossible to arrange an oxidation experiment accordingly. Alternatively, a local effect on flow configuration equivalent to that obtained when the Reynolds Number exceeds the critical value can be obtained by methods described in succeeding sections.

The flow method of oxidation and mixtures of pentane in combining proportions with air, with one exception, were used for the experiments. The 'pentane' was similar to that used for the experiments of Part I and has been described in the appendix to that part. The experimental results for oxidations are given by graphs, moles of oxygen reacted being plotted against temperature. Methods of measuring air and pentane supply and of analyzing oxidation products were as described in the appendix to Part I.

Section II

Flow Configuration and Related Reaction Velocity in Narrow (Packed) Spaces

The ratio of surface to volume is sometimes increased by packing an open combustion space with fragments of the material of the wall, or with lengths of small tubes of the material if a measurable change in the ratio of surface to volume is required. A sufficiently narrow annulus between two coaxial tubes constitutes a packed combustion space and the arrangement facilitates changes of flow configuration. Tubing of invariable diameter and wall thickness is required for an annulus of uniform width over any considerable length and cannot be obtained in glass except by grinding to size. Recourse was had, therefore, to cold drawn steel tubing, which is of uniform inside and outside diameter, and can be had from stock in great variety of size and gauge. Steel possesses the further advantage that wall temperatures can be measured by the use of thermocouples electrically welded into the tubes at desired positions. Mild steel annular reaction spaces of two designs are illustrated by Fig. 1. Design A provides a straight through annulus and Design B a double annulus with communicating orifices in the partition wall at the position of maximum temperature.

Flow Configuration, Single Annulus

Both tubes were 20 gauge (0.036 in.) wall thickness. The inside diameter of the outer tube was 1.1155 in. and the outside diameter of the inner tube 1.0000 in. The width of the annulus was therefore 0.05775 in. or 1.47 mm. and the area of cross section 1.24 cm^2. Gas supplied at 100 cc. per min. would pass through the annulus with a velocity of 1.34 cm. per sec., and at the temperature of supply the flow could not be other than laminar. When, however, the tubes are heated in an electric furnace, the outer attains a higher temperature than the inner and if the tubes are vertical the layer of gas adjacent to the outer wall must rise at a somewhat greater velocity than that adjacent to the inner and cooler wall. Relative motion of the two layers becomes greater

than prevails in purely laminar flow and small eddies form between them. The path of the gas being annular in cross section, the eddy motion would be expected to take the form of vortex filaments moving upward with the gas flow.

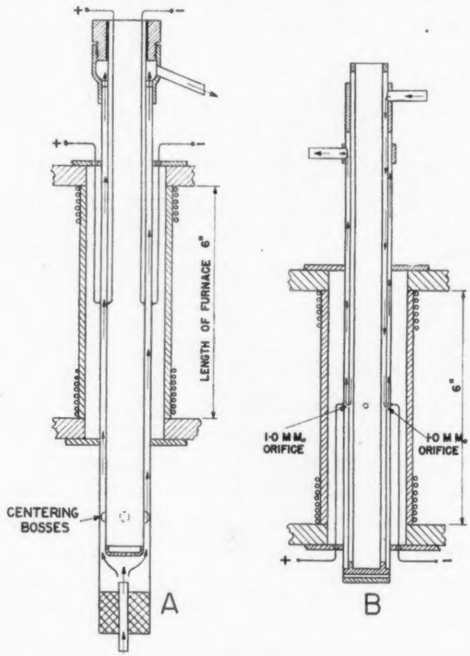

FIG. 1. *Annular combustion tubes (steel).*
A. Single straight through annulus.
B. Double annulus with four orifices in partition.

Flow Configuration, Double Annulus

The double annular combustion space is so arranged that gas entering the inner annulus at the upper end descends to the position of maximum temperature to pass through four 1.0 mm. orifices, equally spaced around the partition wall, into the outer annulus and thence to the exit at the upper end of the apparatus. The design provides an annular combustion space of the same width as that of Arrangement A and of the same length within the furnace but having means for changing flow configuration at the position of maximum temperature. The flow path of the reacting mixture is otherwise similar to that in the single annulus except for the dead space between the cool end and the ring of orifices. The space might have been filled but after preliminary experiments demonstrated the effect of flow configuration on reaction velocity, it appeared that oxidation in the space would be inappreciable as compared with that in the path of the moving mixture. The area of cross section of the inner annulus was 1.32 cm^2, that is, only slightly greater than the 1.24 cm^2

of the outer annulus; flow velocities would, therefore, be approximately equal. The flow configuration may be taken as similar to that in the single annulus except at the position of maximum temperature where the reacting mixture passes through the four orifices. The total area of cross section of the orifices is 0.031 cm^2. and, that of the annulus being 1.24 cm^2., gas velocity through the orifices is 40 times greater than the average through the annular spaces. The relatively high velocity creates a purely local disturbance, breaking down the nearly laminar flow and producing a scouring effect over a small surface area.

Preliminary 'Packing' Experiments

Reaction spaces with steel walls are not generally used for laboratory oxidations and the effect of 'packing' was determined by oxidations in the outer tube used alone and in the single annulus of which the same tube forms the outer wall. The inside diameter of the outer tube was 1.1155 in. and, the length within the furnace being taken as reaction space, surface to volume ratio was 1.49. The ratio for the annular reaction space was 13.6 on the same basis. Pentane–air mixtures in combining proportions were supplied at 200 cc. per min. for both experiments. Reaction velocities are given by the graphs of Fig. 2. It will be noted that reaction in the annulus did not begin

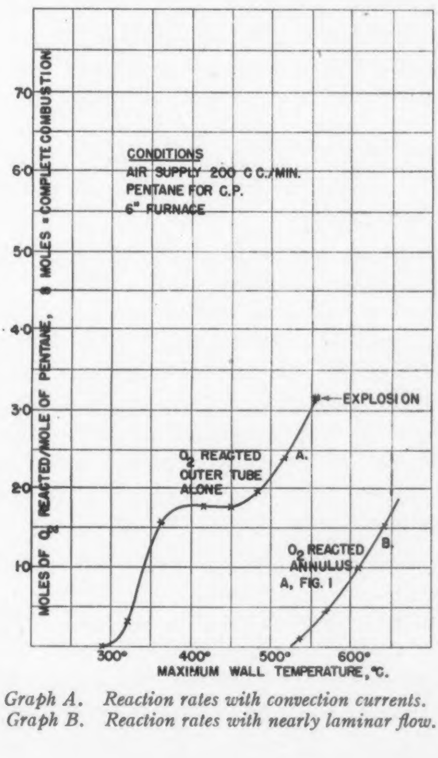

FIG. 2. *Graph A. Reaction rates with convection currents.*
Graph B. Reaction rates with nearly laminar flow.

at a measurable rate until the temperature reached 535° C., which is beyond the range over which partial oxidation products are usually obtained. The final sample was drawn at 640° C. when the tubes were red hot but explosion did not occur. On the other hand oxygen was reacted at an easily measurable rate in the wide tube at 310° C. The rate increased rapidly over the temperature range 310° to 400° C. giving the familiar hump on the graph associated with profuse formation of aldehyde as described in Part I. The reacting mixture exploded at 560° C. The reaction velocities shown by the graphs of the figure *taken at their face value* show that increase in the ratio of surface to volume leads to a reduction in reaction velocity and support the generally accepted view that reaction chains can be initiated or broken on surfaces. It will be shown, however, by experiments described in succeeding sections that the apparent wall effect to reduce reaction velocity is due to flow configuration, not to the breaking of reaction chains.

Reaction Velocity in the Single Annulus as Affected by Change in Flow Configuration Due to Changing Temperature Difference Between Walls

The single annular combustion tube was set up in a vertical furnace as shown at A, Fig. 1. Pentane–air in combining proportions was admitted at the lower end at the relatively low rate of 40 cc. per min. in order that rates of reaction might be greater than determined for the higher rate of 200 cc. per min. The thermocouples at the position of maximum wall temperature indicated that over the range 400° to 600° C. the temperature of the outer tube was on the average 23° C. higher than that of the inner tube. The difference was 27° C. at 400° C. and 18° C. at 600° C. The average temperature difference was reduced to 20° C. by filling the inner tube loosely with asbestos–magnesia to eliminate convection currents.

Rates for reaction for the two conditions are given by Graphs A and B of Fig. 3. It will be noted that the higher rate of reaction, Graph A, is obtained for the greater temperature difference between the walls although the average temperature is the lower. The 15% increase in temperature difference would increase the *relative* velocity of the ascending layers of gas and consequently the size and velocity of the intermediate vortex filaments and the effect on reaction velocity shown by the graphs is quite remarkable. Thus, at 500° C. outer wall temperature rate of reaction increased from 1.8 to 2.4 moles of oxygen or 33% on increasing the temperature difference between the walls by 15%; at 550° C. the rate of reaction increased by 25%.

Reaction Velocity in the Double Annulus as Affected by Change of Flow Configuration at the Position of Maximum Temperature

The double annular combustion tube shown at B, Fig. 1, was set up horizontally in the 6 in. furnace and a mixture of pentane–air in combining proportions was supplied at 200 cc. per min. The average velocity of gas flow through the annular space was, therefore, 2.7 cm. per sec. and 116 cm. per sec.

through each of the four orifices set at the position of maximum temperature. Velocity ratio remains unchanged on heating. The flow configuration at the position of the communicating orifices is, of course, somewhat speculative but it can be calculated from the width of the outer annulus and orifice diameter that the increased velocity of the reacting mixture flowing through any one of the four orifices at one-quarter of the total rate of supply prevails over a disk 6.7 mm. only in diameter. Thus it may be assumed that the otherwise nearly laminar flow became of a turbulent nature over a relatively small area.

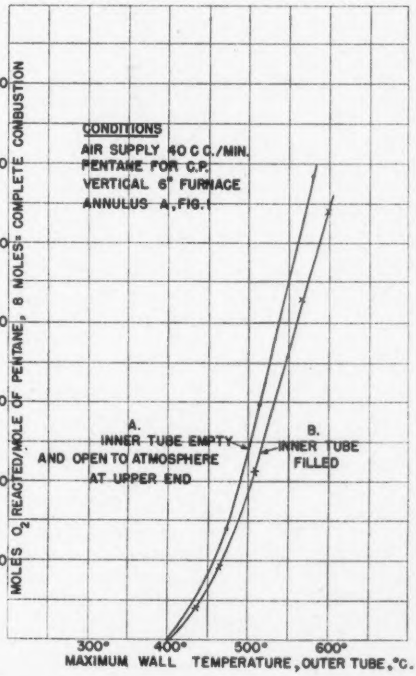

FIG. 3. *Change of reaction rate due to small change of temperature difference between walls of Annulus A, Fig. 1.*

Reaction rate at temperatures rising to over 600° C. are given by Graph A of Fig. 4 and, for convenient comparison, similar rates obtained for the single annulus in which laminar flow was disturbed by temperature difference only are given by Graph B of the figure, together with rates of formation of carbon oxides.

Referring to Fig. 4, Graph A, it will be noted that, (*a*) reaction begins at about 125° C. lower than in the single annulus in which flow configuration is nearly laminar, (*b*) the form of Graph A over the temperature range 400° to 500° C., within which no measurable reaction occurred in the single annulus,

is significant of the formation of partial oxidation products as indicated by the aldehyde hump, (*c*) at temperatures above the 530° C. at which reaction began in the single annulus, oxidation was mainly to the final products, carbon dioxide and steam; at 575° C. the rate was 630% the greater in the double annulus and at 600° C., the greater by 560%.

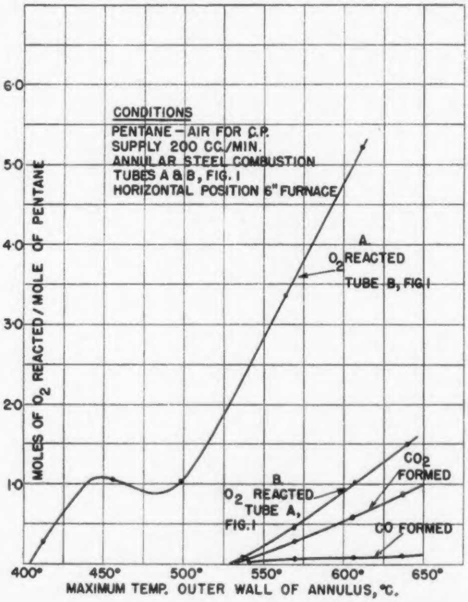

FIG. 4. *Effect of local high mixture velocity on reaction in annulus.*
Graph A. Mixture passing through orifices, double annulus.
Graph B. Mixture passing straight through single annulus.

Section III

Flow Configuration Due to Heat Convection in Unpacked Combustion Spaces and Related Reaction Velocities

A useful purpose will be served by discussing the probable flow configuration due to convection currents in an unpacked combustion tube set up vertically in an electric furnace as shown by Fig. 5. When the tube is heated in the usual manner, maximum temperature is reached by a middle part and there are two temperature gradients with a convection circulation over each. The length of the middle part over which there is no temperature gradient depends on the ratio of tube length within the furnace to tube diameter as well as on the width of the space between the inside wall of the furnace and the tube. The figure illustrates the case of a 1 3/16 in. tube supported in a furnace of 2.0 in. internal diameter and 6.0 in. long. The middle part of the tube, of

uniform temperature, does not exceed 1 in. in length and the ratio $\frac{dl}{dt}$ for the temperature gradients increases as the temperature of the middle part is raised. The lower end of the tube contains cold gas being heated while the upper end contains hot gas being cooled so the value of $\frac{dl}{dt}$ is the greater for the lower of the two temperature gradients. When the temperature of the

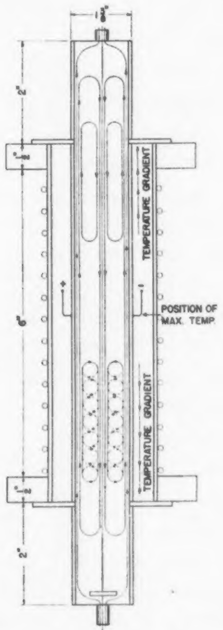

FIG. 5. *Possible flow configuration due to convection currents in vertical combustion tube.*

middle part of the tube is raised to, say, 600° C. it is reasonable to suppose that cool gas entering at rates of 100 cc. per min. and greater can be raised to that temperature in a tube length of about 3.0 in. solely by repeated contact with the hot walls over the length of the lower temperature gradient. Consequently, the corresponding convection circulation tends to break down into a series of eddies taking the form of rising vortex rings as shown dotted on the diagram. A similar effect would be expected in the upper convection circulation but at the higher maximum temperature required for a suitable value of $\frac{dl}{dt}$. When a 'long' furnace is used and the combustion tube is of relatively small diameter the middle part of the tube attains uniform temperature over a considerable length and convection circulations are set up over the end temperature gradients only, but for tubes of relatively small L/D, as illus-

trated by Fig. 5, the descending stream extends throughout the heated length of the tube. The influence of individual variables on the pattern of the flow configuration would be difficult to determine but assuming that the broad outline is as illustrated by Fig. 5, changes can be effected in various ways and the corresponding reaction velocities measured. This section will be completed by describing a number of related experiments.

Effect of Convection Circulation on the Oxidation of Stainless Steel

A stainless steel (18-8, chromium–nickel) combustion tube $1\frac{1}{4}$ in. internal diameter, set up vertically in a 6 in. furnace was used in earlier experiments to demonstrate the explosion of gaseous combustible mixtures by nuclear drops of water (1). The interior wall of the tube was inspected after hydrogen mixed with air in various concentrations had been passed through it. The rate of supply of the mixture was 200 cc. per min. and maximum wall temperatures varied from 620° to 740° C. The bands of brilliant color seen on the wall were so striking that the tube was split and photographed by infrared light. The photograph is reproduced, Fig. 6. The reddish browns appear as whites and the upper band is overemphasized by glare. It will be noted that oxidation of the steel occurred in the upper and lower parts of the tube. The middle part, at maximum temperature, was coated with blue 'heat scale' and some red that could be seen only by viewing the surface obliquely. Many attempts were made to obtain a greater degree of oxidation of the surface at the middle and hottest position, by changes of hydrogen concentration, but without success. It was supposed at the time of the experiments that the direction of motion of the reacting mixture in the tube was always parallel to the longitudinal axis and, on that assumption, the reason for the formation of oxidation bands *both* top and bottom, *and not at the position of maximum temperature,* remained a mystery. The solution of the 'mystery' is obtained, of course, by abandoning the idea of linear flow, assuming that flow configuration is somewhat as illustrated by Fig. 5 and considering that oxidation of appreciable velocity occurs only at wall surfaces subjected to the scouring action of the eddies accompanying convection circulations.

Direction of Gas Flow and Reaction Velocity

The flow configuration due to convection currents in a combustion tube of relatively large diameter would be expected to differ as between the horizontal and vertical positions and be modified by the direction of gas flow when the tube is in other than the horizontal position. Experiments were made accordingly using a Pyrex tube of 1 in. internal diameter and arranging the gas flow to be vertically upwards or downwards or horizontal. The gas was pentane–air in combining proportions, always passed into the tube at 200 cc. per min. The reaction velocities for the three directions of gas flow are given

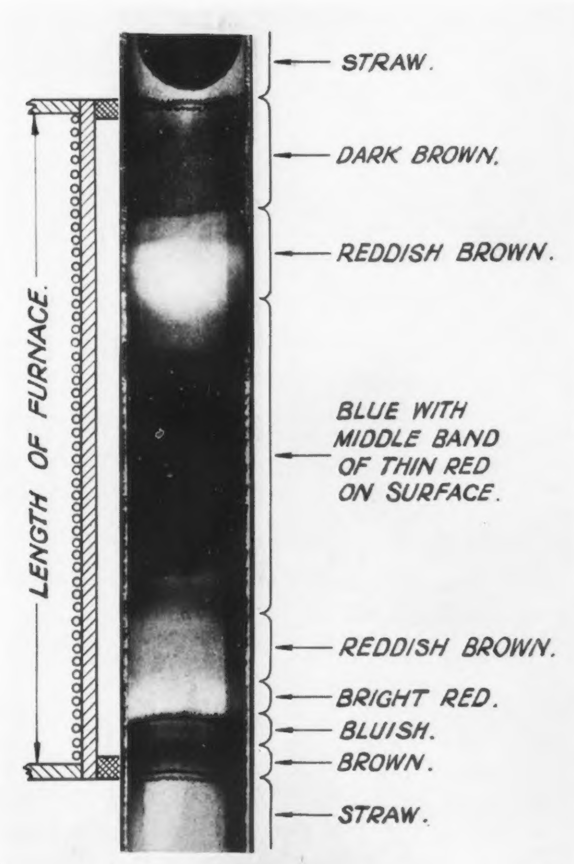

FIG. 6. *Effect of flow configuration on the oxidation of a stainless steel tube.*

by the graphs of Fig. 7. It will be noted that the smallest reaction rate and the lowest explosion temperature were obtained when the gaseous mixture was forced to flow vertically downward. The reaction rate at the temperature of the aldehyde hump increased by 34% on changing the flow from downwards to horizontal and the rate at 550° C. increased by 75% on changing the flow from downwards to upwards.

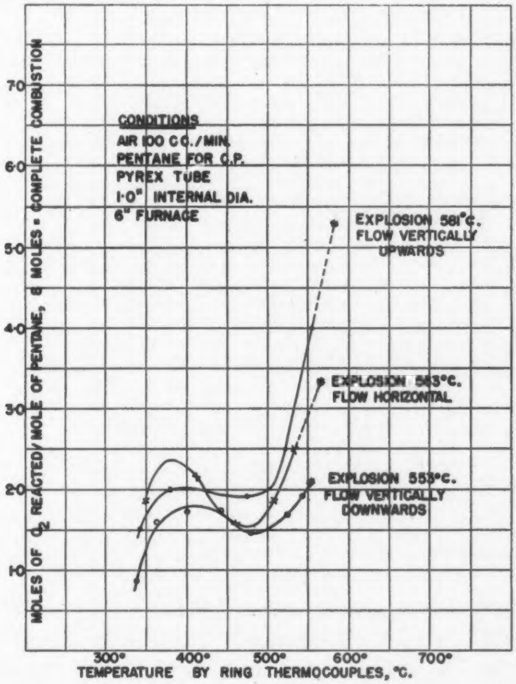

FIG. 7. *Effect of direction of mixture flow on reaction rates in Pyrex tube of small L/D.*

Effect on Reaction Velocity of Changing Entrance Flow Conditions

The usual method of admitting a combustible gaseous mixture to the cool entrance end of a conventional combustion tube is by a small tube projecting through a cork or rubber stopper as shown at B, Fig. 8. An alternative, generally used in the Cambridge experiments, was the distributor inlet shown at A, Fig. 8. Reaction rates were determined for the two types of inlet, pentane–air in combining proportions being admitted in both cases at 300 cc. per min. The internal diameter of the tube inlet was 6 mm. The velocity of the entering stream was, therefore, 17.7 cm. per sec. as compared with 0.85 cm. per sec. average velocity through the larger tube, and the small stream of relatively high velocity, on reaching the lower convection circulation,

would be opposite in direction to the descending central stream. On the other hand, gas admitted through the distributor inlet enters at the periphery of the combustion tube and rises along the heated walls, the direction of motion coinciding with that of the *ascending* stream of the lower convection

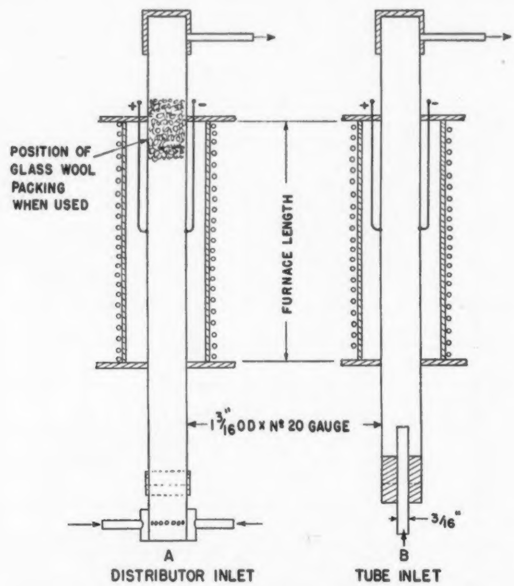

FIG. 8. *Mild steel combustion tube with two varieties of gaseous mixture inlet.*

circulation. Reaction velocities determined in the two conditions are given by the graphs of Fig. 9 for the temperature range of the aldehyde hump and it will be noted that the rate of oxygen reacted at 450° C., when using the tube

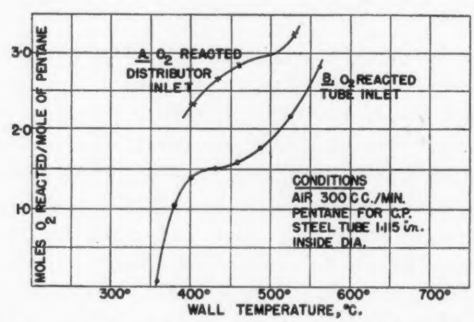

FIG. 9. *Effect on reaction rates of change in lower convection circulation due to change of inlet conditions.*

inlet, was 1.55 moles as compared with 2.75 moles when the distributor inlet was used. That is, the change in flow configuration due to the use of the distributor inlet accounts for nearly 80% increase in reaction velocity at the temperature mentioned.

Effect on Reaction Velocity of Restricting Upper Convection Circulation

The upper convection circulation in a vertical combustion tube can be restricted to some degree by a plug of loosely packed glass wool, as shown at A, Fig. 8. Reaction rates with and without the packing are given by the graphs of Fig. 10. The distributor inlet was used for both experiments and a

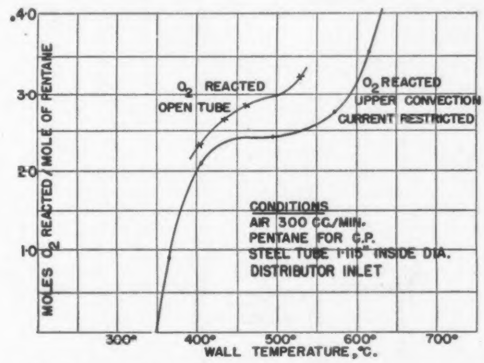

FIG. 10. *Effect on reaction rates of damping upper convection circulation.*

pentane–air mixture in combining proportions admitted at 300 cc. per min. It will be seen by reference to the figure that reaction rate decreased from 3.0 to 2.4 moles of oxygen on restricting the upper convection circulation. The upper circulation is, however, created by the lesser temperature gradient as mentioned earlier and receives partially reacted mixture. Thus, as oxidation of the pentane to aldehyde requires one only of the eight moles of oxygen available, it is probable that reaction accordingly was completed at the position of the lower circulation. The lower reaction velocity at the temperatures of the experiments would, therefore, be expected at the position of the upper convection circulation and change of flow configuration in it would produce less change in the measured over-all reaction rate than if a similar change were made in the lower circulation.

Effect on Reaction Velocity of Changing Flow Configuration in a Single Convection Circulation

The experiments described in preceding paragraphs of this section were made in conditions providing an upper and a lower convection circulation in vertical combustion tubes and 'over-all' reaction velocity only could be determined. The results given below were obtained when using a combustion tube arranged to provide a single circulation extending over the temperature gradient from the middle and hottest part of a vertical combustion tube to the upper end.

The design of the combustion tubes is shown diagrammatically at A and B, Fig. 11. The cool gas of relatively high density admitted at the top of Design A with a velocity of approximately 16 cm. per sec. cannot escape through the outlet without setting up a convection circulation as shown by the diagram.

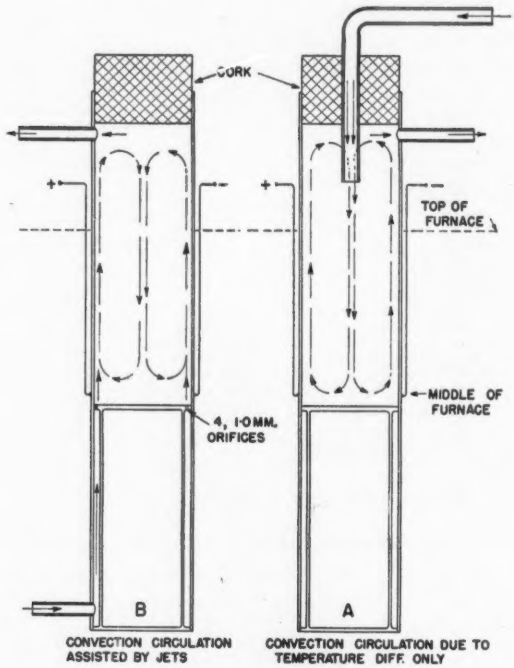

FIG. 11. *Steel reaction chambers in upper half of furnace.*
A. With mixture admitted at relatively low velocity.
B. With mixture admitted by jets assisting convection.

The gas is admitted to Design B at the bottom end and rises through a narrow annulus, in which oxidation is slight, to reach the upper and open space through four 1.0 mm. orifices. The jets issue from the orifices in a position to increase the velocity of the convection circulation already existing by virtue of the temperature gradient but do not impinge on the heated surface of the tube. The odd rate of mixture supply of 167 cc. per min. has no significance.

Reaction velocities determined for the A and B arrangements for pentane–air in combining proportions are given graphically by Fig. 12. It will be seen by reference to Graph A that when flow configuration depended on convection only, the mixture exploded at 600° C. and rate of oxygen reacted never

exceeded 25% of that available. When, however, convection circulation was assisted by the jets, Graph B, reaction was at an extremely high rate but explosion did not occur although the temperature was raised to 660° C. and nearly 95% of the available oxygen reacted accordingly.

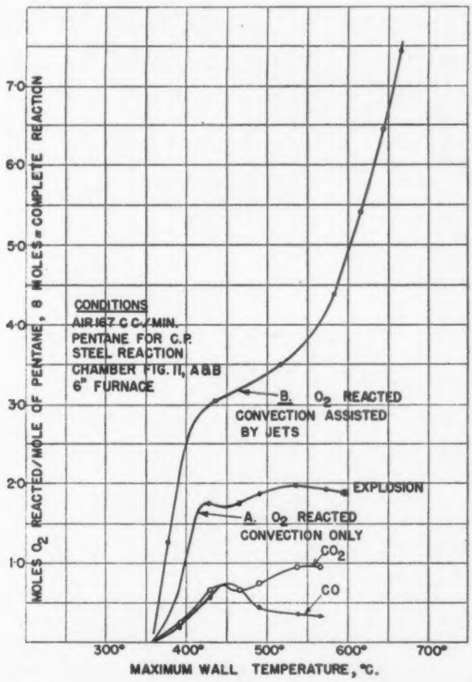

FIG. 12. *Effect of change in convection circulation on reaction rates.*
Graph A. Reaction rate convection only.
Graph B. Reaction rates with jet assisted convection.

Rates of formation of carbon oxides during the pentane oxidation in Design B are given by Graphs B and C of Fig. 13. It will be noted that carbon monoxide formation reached a distinct maximum at 400° C., which has been found to be the temperature of the maximum rate of aldehyde formation. At temperatures of 450° C. and higher, rate of carbon monoxide formation was just measurable, reaction being substantially to the final products, carbon dioxide and steam. The small hump on the carbon monoxide graph at 650° C. might be attributed to error in measurement but it was obtained on several occasions and is believed to be genuine and possibly due to decomposition products that might be present in small proportion in spite of the high rate of oxidation.

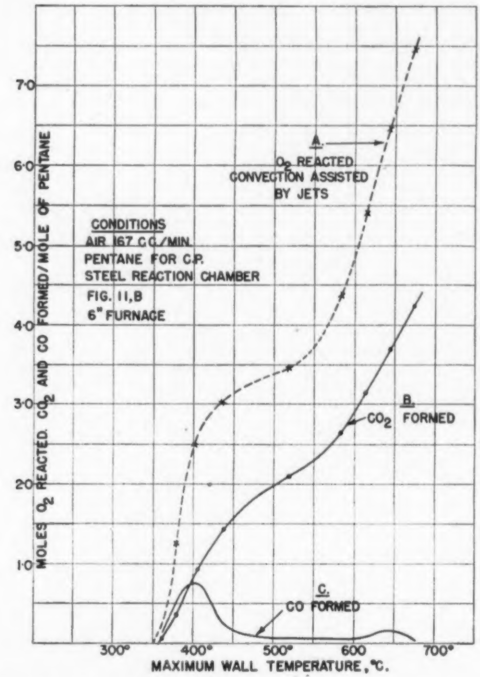

FIG. 13. *Carbon dioxide and carbon monoxide formation in reaction with jet assisted convection circulation.*

Section IV

Reaction Velocity as Affected by the Flow Configuration in Reaction Chamber No. 10

Pentane could be oxidized in Reaction Chamber No. 10 (2) at high velocity and the temperature raised, without the occurrence of explosion, until the reaction of oxygen was complete. The flow configuration within the chamber is, therefore, of interest and is indicated by the diagram, Fig. 14, drawn on an enlarged scale. The diameter of the chamber was 1.2 cm., the length 2.2 cm., and the material Jena Supramax glass. The reacting mixture entering through an orifice at the bottom of the chamber forms a streamline jet that impinges on the top surface of the chamber in suitable conditions of pressure and orifice diameter. The laminar flow in the jet is broken on the surface, the reacting mixture fans out on it and in order to reach the outlet at the bottom periphery of the chamber must move downward along the wall setting up a circulation as shown by the diagram. Eddies as vortex rings probably form between the ascending and descending streams but are not shown by the diagram because the exact flow configuration is speculative. It is important, however, to realize that the velocity of the ascending streamline

jet is greater than that of the stream of gas descending along the wall, in proportion to the respective path areas. The area of cross section of the path of the jet from a 1.0 mm. diameter orifice is 0.0078 cm^2 and that of the return path down the wall, assuming a layer 2.0 mm. thick, is 0.63 cm^2. Therefore, if gas were supplied at the rate of 100 cc. per min. to the unheated chamber, the

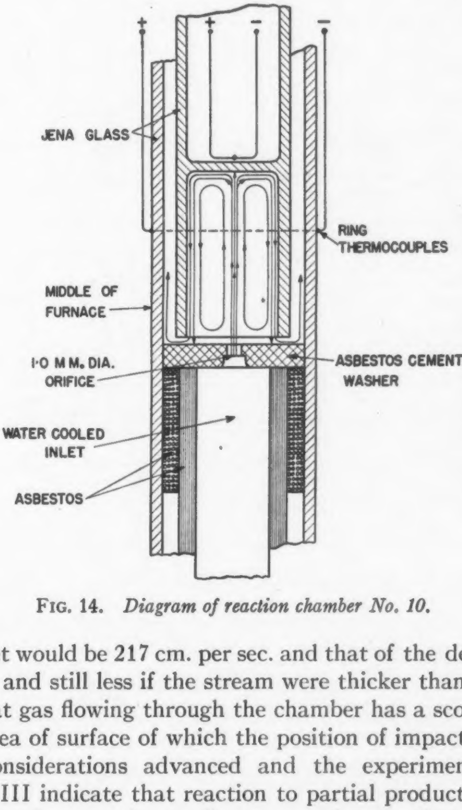

FIG. 14. *Diagram of reaction chamber No. 10.*

velocity of the jet would be 217 cm. per sec. and that of the descending stream 2.6 cm. per sec. and still less if the stream were thicker than 2.0 mm. The conclusion is that gas flowing through the chamber has a scouring effect on a small circular area of surface of which the position of impact of the jet is the center. The considerations advanced and the experiments described in Sections II and III indicate that reaction to partial products proceeds at an appreciable rate only over the small area mentioned, the remainder of the surface of the chamber being of little practical importance. Experiments supporting this view will now be described.

Effect on Reaction Rate of Changing the Velocity of the Jet While Maintaining a Constant Rate of Gas Supply

Pentane–air in combining proportions was supplied at 50 cc. per min., orifice diameters of 1.0 mm. and 0.5 mm. being used. The velocity of the jet from the larger orifice would then be 108 cm. per sec. and that from the smaller one 432 cm. per sec. if the coefficient of discharge were unity. It was verified by separate experiments, using smoke to make the air flow visible, that the jets

retained a streamline form over the distance from the orifices to the position of impact on the top of the reaction chamber. The velocity of the stream of gas descending along the wall would be unchanged and the sole difference in flow configuration would occur in the small circular area of which the position of impact of the jet is the center. Rates of reaction are shown by the graphs of Fig. 15, and it will be seen that on changing from the larger to the smaller

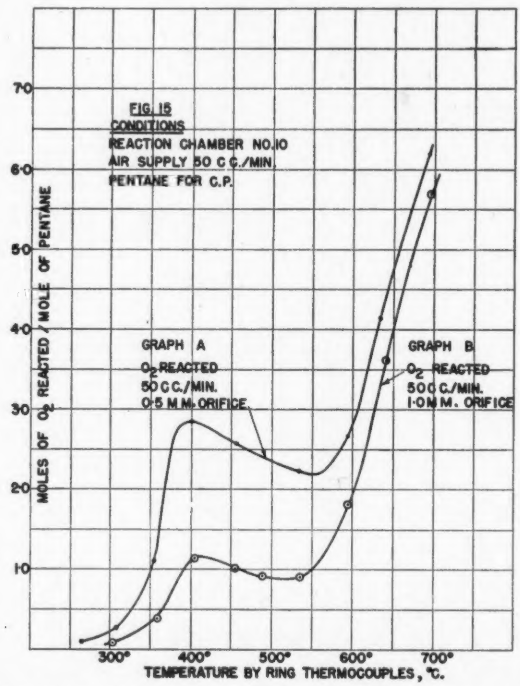

FIG. 15. *Effect of jet velocity, reaction chamber No. 10, with constant rate of mixture supply.*

orifice, reaction velocity increased over the whole temperature range of the experiment. The increase was greatest at the temperature of the formation of partial oxidation products at the maximum rate and was then nearly 150%. It is to be remembered that rate of aldehyde formation was limited because the reacting mixture contained one mole only of pentane to eight moles of oxygen and therefore all of the pentane could be oxidized to aldehyde by the reaction of one-eighth of the available oxygen.

Effect on Reaction Velocity of Increasing the Proportion of Pentane in the Mixture with Air

The graphs of Fig. 16 show reaction velocities for pentane–air supplied to reaction chamber No. 10 through a 1.0 mm. orifice. Graph A gives rates of oxygen reacted when the mixture contained two moles of pentane to eight

moles of oxygen and Graph B gives rates of oxygen reacted when the mixture contained one mole of pentane to eight of oxygen. The experiments were made in similar conditions of flow configuration and of all other respects and show, as would be expected from considerations already discussed, that the

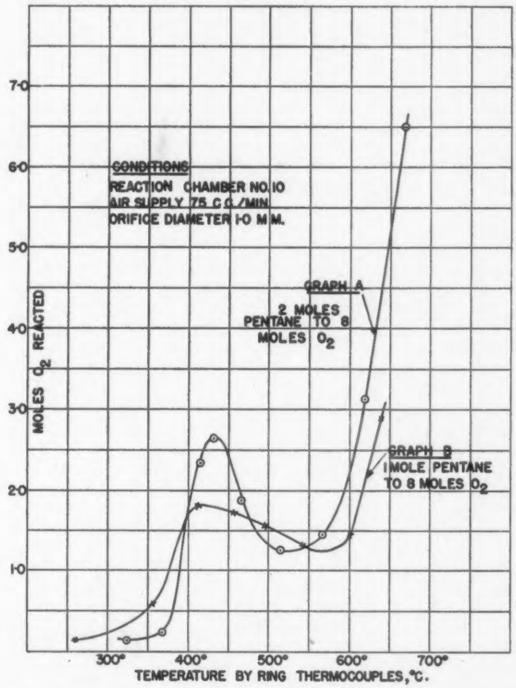

FIG. 16. *Effect of increasing pentane concentration in mixture with air, reaction chamber No. 10.*

removal of partial oxidation products from a relatively small area of active surface by the scouring action of the jet allows access of unreacted mixture and the formation of such products at a greatly increased rate if the composition of the reacting mixture permits. Thus, the aldehyde hump of Graph A is exceptionally pronounced and maximum rate of reaction at the corresponding temperature is 70% greater than for the mixture containing half as much pentane and oxidized in the same conditions of flow configuration.

Effect on Degree of Oxidation of Time of Exposure and Flow Configuration

When a reacting mixture is supplied to reaction chamber No. 10, having a volume of 2.5 cc., at the rate of 50 cc. per min., the time of exposure to the oxidizing conditions, as usually calculated, is 3.0 sec. and the flow configuration is fixed by the diameter of the admission orifice. The rate of supply being increased to 150 cc. per min., the time of exposure is reduced to 1.0 sec.

but if the diameter of the orifice remain unchanged, flow configuration is altered by the velocity of the jet having increased by 300% with a corresponding increase in the scouring effect on the surface on which the jet impinges. The results of experiments made accordingly are given by the graphs of Fig. 17 and it will be seen that over the low temperature range a maximum of

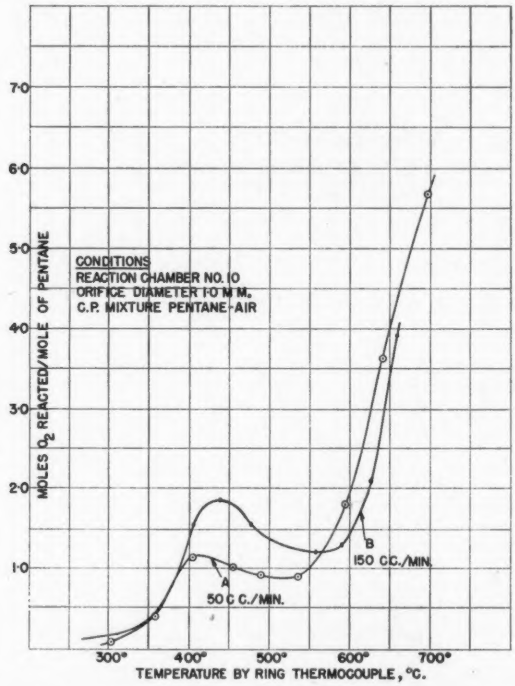

FIG. 17. *Effect of threefold increase in rate of mixture supply, reaction chamber No. 10.*

1.8 moles of oxygen was reacted in the 1.0 sec. exposure time and 1.2 moles only in the 3.0 sec. time. Even over the higher range of temperature for which reaction is mainly to final products the increase of 300% in exposure time accounted for a relatively small decrease in moles of oxygen reacted.

Section V

CONCLUSIONS

The experiments described in preceding sections were concerned with the oxidation of pentane in air but the results are probably of more general application. It is suggested for discussion and for further experimental work—

(*a*) That the reduction in reaction velocity obtained on packing an open combustion space is not due to an increase of surface but to the consequent change in the flow configuration of the reacting mixture.

(*b*) That the oxidation of pentane is a heterogeneous reaction, velocity depending on flow configuration and the nature of the surface of the reaction space. The graphs of Fig. 18 are given in support of the suggestion.

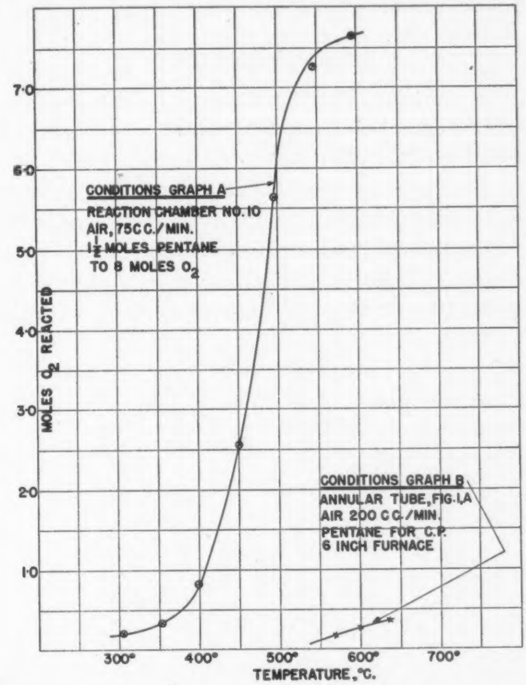

FIG. 18. *Nearly complete or nearly zero reaction depending on flow configuration and nature of surfaces.*

Graph A, showing a remarkable rate of oxidation with completion of the reaction without explosion at 600° C., was obtained for an oxidation in reaction chamber No. 10 of pentane containing iron carbonyl in the concentration of 0.67%. The mixture with air contained 50% more pentane than required for combining proportions. The reacting mixture was, as shown by the experiments of Part I, brought, by the flow configuration in the reaction chamber, into intimate contact with a small surface area of iron maintained in an oxidizing atmosphere by continuous deposition from the carbonyl. In spite of the extremely high reaction velocity, oxidation was, at all temperatures, straight through to carbon dioxide and steam, no more than a trace of aldehyde or carbon monoxide being found in the products.

Graph B was obtained in conditions of nearly laminar flow combined with an inactive surface for a mixture of pentane with air in combining proportions. The steel annular combustion tube A, Fig. 1, was used for the experiment and the surface was rendered inactive in respect of the carbon dioxide steam

reaction by a catalyst poison, ethyl mercaptan, added to the pentane in the concentration of 2%. It will be seen by reference to the graphs that reaction *began* at about the temperature of completion in the conditions used to obtain Graph A, and increased relatively slowly with further increase of temperature.

Acknowledgments

The experimental work described in this paper is part only of that carried out in the Colloid Science Laboratory, Cambridge, with the co-operation of Prof. E. K. Rideal and Dr. F. H. Garner.

The laborious and accurate gas analyses work was undertaken by Mr. R. R. Davidson, Emmanuel College, Cambridge, to whom credit is given for improvements in methods of using the Ambler apparatus.

Dr. E. W. R. Steacie and Dr. L. Marion, both of the National Research Council, have assisted by reading the text and advising accordingly.

References

1. KING, R. O. J. Inst. Petroleum Tech. 20 : 791-820. 1934.
2. KING, R. O. Can. J. Research, F, 25 : 326-342. 1947.

A Continuous Laboratory Vacuum Evaporator

In connection with several projects conducted in these laboratories, it was found necessary to concentrate large volumes of solutions *in vacuo*. A simple, rapid method for doing this was desirable, and a continuous evaporator, designed according to the principle of the rising film vertical tube evaporator (1, 2, 3), and suitable for the concentration of solutions tending to bump or foam, was built. This apparatus has been used extensively for the concentration of aqueous calcium glucopentahydroxypimelate solutions, and butyl acetate solutions of sulphite waste liquor resins.

Apparatus (Fig. 1).—This consists essentially of five parts, the boiler, the catchall, the condensate receiver system, the concentrate overflow (and level control), and the concentrate receiver system. Each part is joined to the

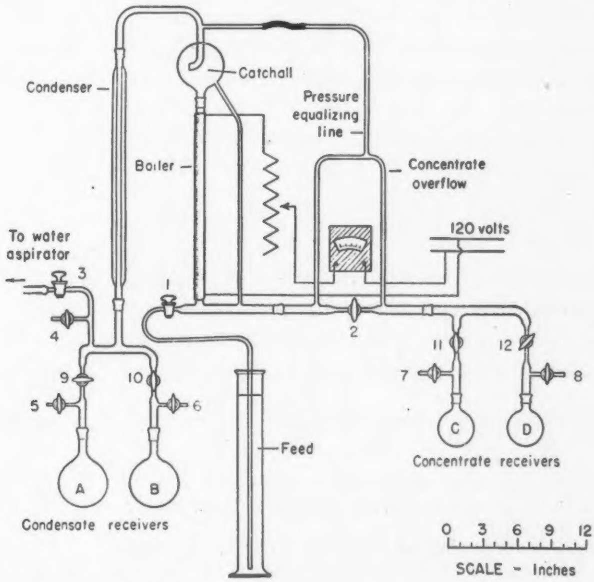

FIG. 1. *Continuous vacuum evaporator.*

next by 24/40 joints. The boiler is tightly wound for its entire height with nichrome wire, insulated with several layers of water-glass impregnated asbestos, and connected externally as indicated to give a power input of from 100 to 200 watts. The boiler is connected at the top, through a 500 ml. catchall, to the condenser, which in turn is connected to the condensate receiver system. The horizontal tube of the evaporator is connected through the concentrate overflow to the concentrate receiver system. By tilting the

latter forward, the level of the feed in the boiler may be varied, so that regardless of the nature of the solution, the evaporator tube is kept wet for its entire height, preventing evaporation to dryness and possible charring at any point in the tube. The entire apparatus is mounted on a board, with the bottom tube at an angle of 10° to 15° from the horizontal to facilitate draining.

Operation.—The apparatus is connected to an aspirator through Stopcock 3, and, with Stopcocks 3, 9, 10, 11, and 12 open and all others closed, the evaporator is evacuated to the desired extent. The vacuum may be controlled by use of a vacuum regulator, or by bleeding air in through Stopcock 4. Stopcock 1 is then opened and feed allowed to enter the apparatus to the desired level in the evaporator tube. Stopcocks 1, 9, and 11 are then closed, and the evaporator tube heated. Boiling begins within one minute, the liquid in the evaporator tube surging into the catchall. Stopcock 1 is opened slightly to permit continuous feed of the liquid, and the level overflow device tilted until a slow but steady amount of concentrate flows over and is collected in Receiver D. It is essential that feed surge into the catchall in order to keep the entire evaporator tube wet, as previously described.

The following data were obtained on the concentration of a butyl acetate resin solution:

Pressure in apparatus—18 mm. Hg,

Temperature of feed entering—20° C.,

Average heat input—136 watts,

Boiling temperature—30° C.,

Volume of butyl acetate evaporated—19.8 ml. per min.,

Area of glass surface—0.25 sq. ft.,

Average power input—136 watts = 1960 cal. per min.,

Latent heat of vaporization of butyl acetate—65 cal. per ml.,

Heating efficiency of evaporator $= \dfrac{65 \times 19.8}{1960} \times 100 = 66\%$.

1. Ames, W. M. Chemistry & Industry, 65 : 194-195. 1946.
2. Mitchell, D. T., Shildneck, P., and Dustin, J. Ind. Eng. Chem., Anal. Ed. 16 : 754-755. 1944.
3. Reavell, B. N. Chemistry & Industry, 65 : 254-255. 1946.

Received June 27, 1947.
Department of Chemical Engineering,
University of Toronto,
Toronto, Ont.

M. Adelman
R. H. Hall